

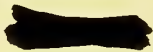


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INORGANIC SEMINARS

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RECENT DEVELOPMENTS OF THE CHEMISTRY OF RHENIUM

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October 3, 1950

In 1947 Pauling (1) listed as one of the unsolved problems of structural chemistry the possibility of the existence of the $-I$ and $+I$ states of rhenium. If uninegative rhenium exists, it would have an electronic structure similar to that of bi-positive platinum ion. Since bipoisitive platinum exists only in complexes of coordination number 4, it would seem probable that $-I$ rhenium would also be found only with four coordinated groups. (Water?) The inorganic seminar of July 23, 1948 by Aaron Herrick (2) was devoted to a discussion of the compounds and oxidation states of rhenium. This seminar continues from that point.

Maun and Davidson (3) have recently completed a study of the oxidation states VII, V, IV, I, and $-I$. Their work represents a material advance in the knowledge of the oxidation states of rhenium.

Re^{VII} : It is known that perrhenate is reduced by stannous chloride to V and IV rhenium. This reduction was followed spectrophotometrically. By this means, it was found that the reduction to V is fast and occurs linearly until two equivalents of stannous chloride have been added. At this point, the formation of a yellow brown substance occurs. After adding three or more equivalents and allowing to stand fifteen hours, the light absorption finally reached a limiting density. From this it is inferred that the formation of Re^V is a slow process, as compared to the formation of Re^V . The solution of Re^V was found to be stable for a period of hours. Agents such as hydrogen peroxide, ceric sulfate, potassium iodate, and chlorine completely oxidized Re^V to perrhenate. Five minutes treatment with oxygen had only slight effect, and molecular iodine caused only a partial oxidation. Mercuric chloride was found to precipitate Re^V . $Re^V + 2HgCl_2 + 4H_2O \rightarrow ReO_4^- + Hg_2Cl_2 + 8H^+ + 2Cl^-$. Attempts to prepare Re^V from 1.9 F HCl failed. In 3F HCl the yield was slightly low. In strong acid (4 F) Re^V is stable, but in weaker acid disproportion takes place. $Re^V \rightarrow Re^{IV} + Re^{VII}$.

Re^{IV} : Solutions of Re^{IV} were only slightly attacked by oxygen or iodine. Ceric sulfate, chlorine, and iodate ion caused a complete oxidation to perrhenate ion. Chromous ion reduced perrhenate ion to Re^{IV} . Re^{IV} in excess HCl gave $ReCl_6^-$. The hexachlororhenate ion was found to be inert to oxygen, stannous chloride, iron II and III, iodine, potassium iodide, potassium iodate, and copper I and II. Hot ceric sulfate caused a complete oxidation of $ReCl_6^-$ to

perrhenate ion. Cs_2ReCl_6 was found to be insoluble, and hence it could be used in determining ReCl_6^- . Evidence from absorption curves points to the existence of two or more forms of Re^{IV} in solution. It is hypothesized that the yellow-brown Re^{IV} differs from hexachlororhenate ion in the presence of Re to O bonds and Re to Cl bonds in the former while in the latter only Re to Cl bonds are present. The following facts are cited as evidence:

- Re^{IV} from ReO_2 and HCl is converted to ReCl_6^- simply by heating the acid solution.
- The yellow Re^{IV} is formed only from oxygen containing compounds.
- Comparison of the color of ReO_2 and the two different Re^{IV} ions.
(One similar, one distinctly different.)

It is supposed that a series of hydroxo ions $\text{ReCl}_{6-n}(\text{OH})_n^-$ or a series of polymers with rhenium to oxygen to rhenium bonds exists.

$\text{Re}^{-\text{I}}$: $\text{Re}^{-\text{I}}$ was first prepared by Lundell and Knowlen (4). It was obtained in a solution that exhibited the characteristics of the halides. The preparation was accomplished by passing a cold, dilute solution of potassium perrhenate acidified with sulfuric acid through a Jones reductor. Titration with potassium permanganate and other oxidizing agents was used to determine the oxidation number. Maun and Davidson (3) used essentially the same procedure. A hydrochloric acid solution was employed, and cerium^{IV} was used to titrate the $\text{Re}^{-\text{I}}$. Acid strength, amalgam concentration, and total volume were not critical. Initial concentration of Re^{VII} was critical; no concentration larger than 0.0001 could be employed. Inert atmosphere was a necessity. Iodate ion oxidized $\text{Re}^{-\text{I}}$ to Re^{VII} quantitatively, iodine almost quantitatively. Solutions of $\text{Re}^{-\text{I}}$ are colorless. These workers could not prepare a carbonyl of $\text{Re}^{-\text{I}}$.

$\text{Re}^{+\text{I}}$: Noddack and Noddack (5) describe a solution of $\text{Re}^{+\text{I}}$, but present no analyses or proof. Lundell and Knowlen (4) prepared $\text{Re}^{+\text{I}}$ by heating the sulfuric acid solution of $\text{Re}^{-\text{I}}$. Maun and Davidson (3) used $\text{Cu}^{+\text{I}}$ to oxidize the $\text{Re}^{-\text{I}}$ to $\text{Re}^{+\text{I}}$. (Excess $\text{Cu}^{+\text{I}}$ further oxidizes the $\text{Re}^{+\text{I}}$). Bubbling oxygen through solutions of $\text{Re}^{-\text{I}}$ caused the rapid formation of a brown color. The change in titre corresponded to the oxidation of $\text{Re}^{-\text{I}}$ to $\text{Re}^{+\text{I}}$. Further oxidation was slower. The addition of perrhenate solution to a solution of $\text{Re}^{-\text{I}}$ gave $\text{Re}^{+\text{I}}$ within thirty minutes. Re_2O has been reported in the literature (6), as has $\text{Re}^{+\text{I}}$ from the reduction of $\text{ReCl}_6(\text{Re}_2\text{Cl}_6)$. (7)

The isotopes of rhenium: F. W. Aston (8) first identified the natural isotopes of rhenium. Isotopes 185 and 187 were detected in an abundance of 1:1.62. The first radioactive isotope of this element was reported in 1935⁽⁹⁾. This was an activity produced by the bombardment of rhenium with neutrons and was later identified as Re¹⁸⁸ (10).

Re¹⁸² : Re¹⁸² was produced from ^{tantalum} tungsten by neutron bombardment⁽²⁰⁾. Half Life: 2.67 ± 0.002 days. β^- emitter., K or I.T.

Re¹⁸³ : Re¹⁸³ was also produced from tantalum. Half Life: (21) ~~0.53 ± 0.008~~ days. β^- emitter, K or I.T. *~ 240 days*

Re¹⁸⁴ : Re¹⁸⁴ was similarly produced from tantalum (21). It was also produced from rhenium by neutron bombardment and by deuteron bombardment of tungsten (12). Half Life: 50 ± 2 and 2.2 ± 0.1 days. β^- emitter, K or I.T. W¹⁸³ (d,n)Re¹⁸⁴

Re¹⁸⁵ : Naturally occurring.

Re¹⁸⁶ : Re¹⁸⁶ was produced by slow neutron bombardment of rhenium (10). Its identity was proven by Hess, Hayden, and Ingraham (15). Half Life: 92.8 hours.

Re¹⁸⁷ : A metastable state of this element results (13) from the decay of W¹⁸⁷. The transition has associated with it an energy of 0.130 mev. (See Schwartz and Pool (14)) W¹⁸⁷ \rightarrow Re¹⁸⁷ + β^- . Although the element was originally not thought to be radioactive, it is known now that it is a β^- emitter with a half life of $4 \pm 1 \times 10^{12}$ years. (18) Re¹⁸⁷ \rightarrow Os¹⁸⁷ + β^- (19)

Re¹⁸⁸ : The half life of this isotope has been accurately determined to be 18.9 hours (16).

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CATALYSIS OF OXIDATION-REDUCTION REACTIONS¹

Carl E. Johnson

October 10, 1950

Although much has been done toward elucidating the mechanisms of individual oxidation-reduction reactions, the necessary electron and atom transfers and the factors affecting the rates of reaction are still not well understood. In this general field we were interested in the problem of catalysis of oxidation reduction reactions by quinones and similar materials, qualitative reports of which have appeared a number of times.

For example, Bela Gaspar² has reported that the reductive cleavage by colloidal silver of ozo-dyes in hydrochloric acid solution is effectively catalyzed by as little as one part in 100,000 of 2,3-diaminophenazine, 2-hydroxy-3 aminophenazine, quinoxaline, 2,3 diphenylquinoxaline, and many other substances including some with the anthraquinone and methylene blue type of structure. Similarly³, the reductive cleavage of methyl orange by titanous chloride in hydrochloric acid solution is catalyzed by 2-hydroxy-3-aminophenazine. Further, P. A. Shaffer⁴ has reported the reduction of iodine by titanous chloride in hydrochloric acid solution to be catalyzed by indigo sulfonates, pyocyanine, phenazines, rosindulin, flavins, indophenols, and anthraquinone and naphthoquinone sulfonates.

Much of the previous thinking with regard to this kind of catalysis has centered around the fact that almost all of these compounds have been shown by Michaelis⁵, Preisler⁶, and others⁷ to be capable of reversible two step oxidation-reduction by way of semiquinones. Catalysis is supposedly due to the incursion of reaction steps faster than the uncatalyzed one, involving various of the catalyst species and the reducing or oxidizing agent. Proponents of the "Principle of Compulsory Univalent Oxidation", which owes its name to Michaelis⁸ but was first suggested by Haber and Weiss⁹, would make these steps necessarily one electron changes. P. A. Shaffer, on the other hand, with his "Principle of Equivalence Change"^{4,10} supposes that the role of the catalyst in such reactions is to provide a system which, by virtue of its three oxidation states, can react rapidly with both two-electron and one-electron reagents. For the iodine-titanous ion case, iodine and titanous ion were presumed to be two-electron and one-electron reagents respectively.

Because the titanous, chloride-iodine reaction has a convenient rate, is catalyzed by a wide variety of substances, and is easily subject to kinetic study by methods developed

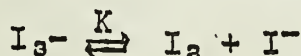
by Yost and Zabaro¹¹, it was chosen for use in our study of the role of quinones and similar substances in the catalysis of redox reactions.

Since we were interested in making use of this reaction over a more extended range of reagent concentrations and temperature than was covered by Yost and Zabaro¹¹ we found it necessary to repeat and extend some of their work.

Measurements of the rate of reaction by chemical means and graphical analysis of the results lead to the rate law

$$-d(I_3^-)/dt = k_1'(Ti^{III})(I_3^-)/(H^+)(I^-) + k_2'(Ti^{III})(I_3^-)/(H^+) + K'(Ti^{III})/(H^+)$$

the first two terms on the right being the more important except at very low triiodide concentrations. In the acid and iodide ion concentration ranges employed, between 1 and 0.1 M, and at an ionic strength of 1, 0.2 the equilibrium



is known to lie far to the left, K being equal to .0041. Also we have assumed the equilibrium



to lie far to the left. These assumptions allow several mechanistic interpretations of the k_1' term of the rate-law, one of which is represented by the following sequence.

1. $TiOH^{++} + I_2 \xrightarrow{\text{Slow}} TiO_2^{+2} + H^+ + I_2^-$
2. $I_2^- + TiOH^{++} \xrightarrow{\text{Fast}} TiO_2^{+2} + H^+ + 2I^-$
3. $I_2^- + I_2^- \xrightarrow{\text{Fast}} I_3^- + I^-$

From the values of $k_1' = (.0545 \pm .0012)$ mole/liter⁻¹ min.⁻¹ and $k_2' = (.0640 \pm .0073)$ min.⁻¹ and the equilibrium constant $K = .0041$, it may be calculated that $TiOH^{++}$ reacts a little more than 200 times as fast with I_2 as it does with I_3^- .

Similar methods of experiment and analysis of catalyzed reactions indicated three general types of catalytic mechanism in operation. Indigo carmine catalysis at concentrations as low as 10^{-7} was described by the rate-law

$$-d(I_3^-)/dt = k (Cat)(I_3^-)$$

neglecting the influence of hydrogen and iodide ion concentration. Pyocyanine and alpha-hydroxyphenazine at concentrations as low as 10^{-5} to 10^{-6} M resulted in the rate-law

$$-d(I_3^-)/dt = k(Cat)(Ti^{III})$$

While beta-hydroxyphenazine and anthraquinone beta-sulfonate at concentrations of about 10^{-5} M catalyze according to the rate-law

$$-d(I_3^-)/dt = k_1(Cat)(Ti^{III})(I_3^-) + k_2(Cat)(Ti^{III})$$

where the first term on the right is of equal or greater importance than the second.

We thus see that Indigo carmine appears to catalyze by a mechanism involving a rate-determining reduction of iodine by the catalyst, alpha-hydroxyphenazine by a mechanism involving a rate-determining oxidation of Ti^{III} by the catalyst, while beta-hydroxyphenazine and anthraquinone beta-sulfonate operate in an entirely unexpected manner which seems to involve a transition state composed of one molecule of catalyst, one of reducing agent and one of oxidizing agent. In the case of the anthraquinone independent determinations of the relative rates of reduction of the quinone by Ti^{III} and the oxidation of the hydroquinone by iodine have shown the oxidation to be much the more rapid. This fact leads to the conclusion that the catalyst molecule involved in the transition state is in the fully oxidized condition and suggests that its only function may be to act as an electrical conductor in facilitating the transfer of an electron from a Ti^{III} to an iodine molecule.

1. This work was carried out under the direction of Prof. S. Winstein at the University of California at Los Angeles. The portion described here is abstracted from the speakers Ph. D. dissertation, dated June 1950.
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ALPHA RADIOACTIVITY AND THE STABILITY OF HEAVY NUCLEI

A. M. Ross

October 17, 1950

I. Perlman (1) has discussed alpha-decay theory from both a qualitative and a quantitative view. He has presented several important advances which have been made in the last few years toward completing the picture of stability of heavy nuclei and predicting structures of unknown species.

Early Developments in Alpha-Decay Theory

The well-known alpha-scattering experiments of Rutherford, in which large angle scattering of alpha particles directed at heavy atomic nuclei was observed, implied that a potential barrier several times higher than the energies of the alpha particles must be assumed to surround the nucleus. While this explained why the alpha particles could not enter the nucleus it did not explain how the alpha particles circumvent this barrier in leaving a heavy nucleus (alpha-disintegration). The answer came simultaneously in 1928 from Gurney and Condon (2) and from Gamow (3) who used the then new quantum mechanics to explain how the wave nature of a particle allows it a finite probability of penetrating a region forbidden to it by classical theory.

The alpha particle within the nucleus encounters the barrier about 10^{20} times each second and eventually finds its way through, while a particle outside has only a very small chance of getting through the barrier in its single fleeting contact as it flies by. Parenthetically, it may be pointed out that one of the important functions of a particle accelerator, such as a cyclotron, is to bring charged particles to energies that will allow them to go over the potential barrier and thus reach within the nucleus at will.

Detection and Identification of Alpha Particles

Of far reaching, practical importance is the fact that an alpha emitter gives off monoenergetic particles whose energies may be measured very precisely. This makes it possible not only to detect but also to identify fantastically small numbers of atoms (a few thousand atoms) by measuring the energies of their alpha particles.

This may be accomplished by use of the recently developed alpha-pulse analyzer (4) which under favorable conditions (no other alpha-emitters of close to the same energy as the one under consideration), may detect and identify an alpha emitter which decays at a rate as low as 0.001 disintegrations per second. When large quantities of alpha emitters are available, their energies may be determined to within 0.1% by use of the alpha-ray spectrometer (5). In the case of artificially produced alpha-emitters, the quantities prepared are usually insufficient for use with the alpha ray spectrometer. The pulse analyzer is used instead. In addition to the fact that it can perform spectrometry on weak sources, the alpha-pulse analyzer has the advantage of speed which is of paramount importance in the measurement of short-lived alpha-emitters.

A great number of nuclides in the heavy-element region are formed by alpha-decay chains. By measuring the energies, one has an accurate thermodynamic scale relating the stability of different nuclei and by mapping trends in stability, one not only learns something of nuclear structure but may also predict properties of unknown nuclei by interpolation and extrapolation.

Systematics of Alpha Energies (6)

If alpha energies are plotted against mass number for each of the heavy elements, it is found that the isotopes of each element define an essentially linear curve showing an increase in alpha energy with decreasing mass number and that the curves for the different elements are roughly parallel.

From these curves, it is possible to estimate energies of unknown species, and, as will be shown, the half-lives may be calculated from the energies.

Alpha-Decay Half-Lives (6)

The model on which alpha-decay theory is based considers the alpha particle to exist as an entity within the nucleus of its decay product, and its rate of emission is governed by its emission velocity and the potential barrier of that nucleus. The height and thickness of the barrier are a function of nuclear charge and nuclear radius which operate to increase the barrier when there is an increase in charge or a decrease in radius. There is no provision in this one-body model for the assembly of the components of the alpha particle during or before its emission.

If it is assumed that nuclear radius is related in a simple fashion to the number of nucleons (e. g., $r = 1.48 \times 10^{-13} A^{1/3}$ cm. where A is the mass number), a series of curves may be calculated in which the logarithm of the half-life is plotted against the alpha energy, each curve denoting constant atomic number.

When experimental data for energy and half-life of the even-even nuclei (even numbers of protons and neutrons) are compared with the calculated curves, the agreement in general is extremely good.

While the even-even nuclei appear to obey the one-body theory of alpha decay, it is found that other types such as the even-odd nuclei do not. Indeed, they have abnormally long half-lives which are explained by the theory that nuclei having an odd nucleon may not be considered as having a preformed alpha particle, but that, instead, time is required to assemble the components.

Prediction of Heavy-Element Properties

The value of the correlations discussed above lie partly in the insight they afford into the structure of heavy nuclei and the theory of the alpha-decay process, but are also extremely useful in giving a rational basis for prediction of radioactive properties of unknown species.

For example, before the discovery of Californium, it was possible, by extrapolation of alpha-energy-versus-mass-number data and checking by other empirical plots, to predict that the alpha energy of Cr^{244} should lie in the range 7.1 - 7.3 Mev. At this energy, this even-even nucleus should have a half-life of 0.3 to 2 hours. When finally isolated, Cr^{244} was found to have an alpha energy of 7.25 Mev and a 45 minute half-life (7).

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THE HALOGEN FLUORIDES

Robert F. Vance

October 24, 1950

Introduction:

The interhalogen compounds compose a unique series. One might suppose that it is limited to diatomic molecules. However, this is only one subdivision of the general type AB_n , where $n = 1, 3, 5, \text{ or } 7$. In all, eleven interhalogen compounds are known, being practically non-associated and essentially covalent molecules. The types AB_5 and AB_7 have appreciable ionic character, since iodine and bromine are considerably less electronegative than fluorine. All are prepared by direct combination of the elements, a few having also been prepared in other ways. In no case are more than two halogens present and there is never more than one atom of the heavier element. The latter limitation appears to be a result of steric factors, for when $n > 1$, $B = Cl \text{ or } F$ and when $n > 3$, $B = F$. Among the AB compounds the greater the difference in size between A and B the less stable is the compound. Thus iodine fluoride is unknown and bromine fluoride is less stable than chlorine fluoride.

This was explained by Sidgwick (14) on the basis of heats of linkage. Nearly all the heats of linkage between halogens are of about the same magnitude. Thus a reaction involving an increase in the number of links, e.g., $AB + B_2 \rightarrow AB_3$, is exothermic and the new interhalogen compound is the more stable. For this reason the interhalogen compounds have a tendency to disproportionate into free halogen and an interhalogen containing an atom of higher valence. This behavior is limited by steric factors, iodine heptafluoride being the only interhalogen of type AB_7 . A summary of the known interhalogens is given in Table I.

TABLE I

	<u>AB</u>	<u>AB₃</u>	<u>AB₅</u>	<u>AB₇</u>
Cl	ClF.	ClF ₃		
Br	BrF, BrCl	BrF ₃	BrF ₅	
I	ICl, IBr	ICl ₃	IF ₅	IF ₇

The developments of the Manhattan Project gave fluorine chemistry a tremendous impetus, particularly in the field of organic fluorides. Elemental fluorine, being an extremely

corrosive gas which must be confined under pressure, is very inconvenient to handle, so many indirect fluorinating agents have been investigated. Research groups under Emeléus in England and Schumb and Lord in this country have studied the applications of the halogen fluorides. In general they possess nearly the same fluorinating power as elemental fluorine, but their different physical properties alter the technology, making it easier in some cases (9).

TABLE II

	<u>m.p.</u>	<u>b.p.</u>
IF ₇	5-6°	Subl. 4.5°
IF ₅	-8°	97°
BrF ₅	-61.3°	40.5°
BrF ₃	-8.8°	127.6°
ClF ₃	-83°	11.3°
BrF	-33°	20°
ClF	-154°	-100.8°

IODINE HEPTAFLUORIDE

Iodine heptafluoride is unique in that it is the only binary compound in which seven-fold coordination is displayed. The structure has been shown by recent infra-red and Raman spectral studies to be pentagonal bipyramidal (8).

It is prepared by combination of fluorine with iodine pentafluoride at 280°C. There is no evidence of salt formation (MIF₈) with alkali fluorides (3). Studies of the reaction with various Freons have been made. Infra-red spectra reveal no fluorination of chlorotrifluoromethane. At 370°C. the conversion of dichlorodifluoromethane proceeds to give a 9% yield of chlorotrifluoromethane. Addition of mercuric fluoride catalyst increases the yield to 68%. This gives a higher yield than when mercuric fluoride is used alone.

Elemental fluorine reacting with dichlorodifluoromethane produces only a small percentage of chlorotrifluoromethane. Thus it would appear that iodine heptafluoride is a more potent fluorinating agent than fluorine itself; this may be due to catalytic action of iodine.

IODINE PENTAFLUORIDE

Reaction of iodine pentafluoride with iodoform yields fluoroform (CHF_3) as the major product (1). Thus it is seen that iodine pentafluoride is not a sufficiently powerful fluorinating agent to remove the hydrogen of fluoroform. Carbon tetraiodide is completely fluorinated by iodine pentafluoride, the product being perfluoroethane. Trifluoroiodomethane is readily obtainable by treatment of carbon tetraiodide and tetraiodoethylene yields pentafluoroiodoethane. Emeléus (3) reports that potassium fluoride dissolves in boiling iodine pentafluoride with formation of potassium hexafluoroiodate (V). This is the only known salt of the type MIF_6 .

BROMINE PENTAFLUORIDE

Combination of gaseous bromine with fluorine at 200°C . produces bromine pentafluoride. It appears probable that bromine pentafluoride reacts with every known element except nitrogen, oxygen, and the rare gases (2). There is no recorded instance of a desired organic fluoride being obtained by use of bromine pentafluoride.

BROMINE TRIFLUORIDE

Bromine trifluoride may be obtained by bubbling fluorine through liquid bromine (5). Some inorganic halides form salts (12) in bromine trifluoride as a solvent, e.g., KBrF_4 , $\text{Ba}(\text{BrF}_4)_2$. Many others undergo conversion to the simple fluorides. The formation of complex salts is supported by the following facts:

- 1). Powder X-rays do not indicate potassium fluoride but show new lines.
- 2). Bromine trifluoride reacts vigorously with carbon tetrachloride and explodes with acetone. Potassium tetrafluorobromate (III) (KBrF_4) does neither.
- 3). Even boiling bromine trifluoride doesn't attack platinum, while potassium tetrafluorobromate (III) corrodes it badly.
- 4). The specific conductance of bromine trifluoride at 25°C . is 8×10^{-3} mhos and may be explained by assuming the existence of the ions BrF_2^+ and BrF_4^- . Chlorine trifluoride, which shows no salts of this type, has zero conductivity in the liquid state.

Sharpe (13) has reported reactions employing bromine trifluoride as a parent solvent. Gold (III) hexafluorobromate ionizes in solution to BrF_2^+ and AuF_4^- . An acid according to the solvent system theory, it reacts with a solvent system base:



The English group also studied the fluorinating properties of bromine trifluoride on tetrahalomethanes and tetraiodoethylene (1). A mixture of halomethanes is obtained. Carbon tetraiodide yields dibromodifluoromethane and carbon tetrafluoride (11). Chlorocarbons may be partially fluorinated with bromine trifluoride (6,7); then completed by Fowler or Swarts reactions, e.g., C_2Cl_6 to C_2F_6 .

CHLORINE TRIFLUORIDE

Chlorine trifluoride can be prepared from the elements. It is less stable at higher temperatures, there being an equilibrium



Production of pilot plant quantities of chlorine trifluoride was reported in Germany during the war (10). Apparently the German army was considering it for anti-aircraft and anti-tank shells because of its incendiary action. It is now available in this country on a commercial scale. Many metals can be fluorinated by chlorine trifluoride in a steel-lined autoclave (4). Only chromium and V2A-steel have been found resistant. Most organic materials (even high vacuum oils) ignite spontaneously in contact with chlorine trifluoride.

BROMINE FLUORIDE

Bromine fluoride (BrF) has never been prepared in higher than 50% concentration. Booth and Pinkston are not convinced of its existence (2).

CHLORINE FLUORIDE

Chlorine fluoride (ClF) appears to react with all metals, differing only in the ease of reaction. This is due, in large part, to the stability of the fluoride films (2). It also is extremely reactive with non-metals and inorganic salts. No controlled reactions with organic materials have been noted.

SUMMARY

While little of a practical nature has yet been uncovered concerning the reactions of the halogen fluorides, some of them possess definite advantages over elemental fluorine as fluorinating agents and may soon be used for that purpose.

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REACTIONS OF INORGANIC SUBSTANCES WITH SOLUTIONS OF METALS IN LIQUID AMMONIA

Perry Kippur

October 31, 1950

INTRODUCTION

Although solutions of metals in liquid ammonia and certain simple amines have long been known and have been the subject of numerous investigations, the field as a whole remains relatively unexplored. This is especially true with respect to inorganic substances. Furthermore, practically no studies of these solutions have been carried out in the regions of high concentration and elevated temperatures (i.e. above room temperature).

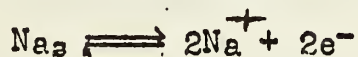
Liquid ammonia solutions of metals have become increasingly important in the synthesis of organic compounds, particularly those in a highly reduced state. In the field of inorganic chemistry, metal-ammonia solutions are of prime interest because of their effectiveness as powerful reducing media. In addition, these solutions offer an experimental approach to the study of intermediate stages of reduction.

Liquid ammonia possesses several distinct advantages in comparison to water as a medium for reduction reactions. In water, only reducing agents less powerful than hydrogen may be used or else hydrogen will be liberated from the water. While ammonia on the other hand, permits the use of powerful reducing systems, such as, the alkali and alkaline earth elements over a wide range of concentration and temperature. Furthermore, in the absence of catalysts, the rate of reaction of ammonia with the metals dissolved in it is negligible in comparison to most of the rates of reaction in which these solutions participate. Still further, liquid ammonia, because of its low autoionization, permits the preparation and study of materials which undergo hydrolysis in aqueous solution.

The low boiling point and extreme hygroscopicity of liquid ammonia requires the use of more elaborate equipment and somewhat more involved manipulative technique. These factors may be considered as disadvantages in comparison to solvent systems, such as water, but these difficulties are easily overcome. It should be remembered however, that the optimum conditions for the use of liquid ammonia require the complete exclusion of moisture from the atmosphere.

The exact nature of these metal in ammonia solutions is not known, but in the light of our present knowledge, the results of numerous physical measurements are in fair agreement with the following assumptions:

a. In concentrated solution one may consider the following dissociation to take place:



However, these electrons have the same mobility which they possess in a solid and this in turn gives rise to abnormally high conductance.

b. Upon dilution, the above reaction is accompanied by the solvation of the electrons.



The mobility of the ammonated electron is much less than that of the free electron. This solvation increases with dilution and the conductance becomes more truly electrolytic.

The solutions of metals in liquid ammonia are quite stable, considering the extreme reactivity of the alkali and alkaline earth elements in such solvents as water and alcohol. (Solutions of sodium in liquid ammonia are stable for two weeks in the absence of catalysts). Such materials as iron oxide, finely divided platinum, metal amides and ultraviolet light act as catalysts for the decomposition of these metal in ammonia solutions.

The metals that are soluble in liquid ammonia include the alkali metals, calcium, barium and strontium. (Magnesium and aluminum are soluble under special conditions).

The ability of liquid ammonia solutions of the metals to readily and rapidly reduce many substances may be explained on the basis of the following:

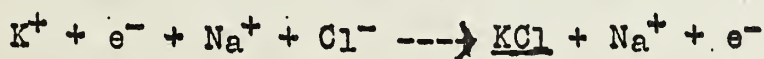
a. Availability of "electron-ions" (reduction involves addition of electrons).

b. Infinite surface area, since the metals are in solution.

c. Low reactivity of the solvent toward the dissolved metal.

The process of reduction in metal ammonia solutions involves the addition of one or more electrons to an atom, ion or group of atoms. The metal cation present usually does not influence the course of the initial reduction process.

The reduction of a positive ion usually leads to the formation of a neutral atom or group as the primary reduction product e.g.



However, this type of reaction is determined almost entirely by solubility relationships. Another type of positive ion reduction takes place in the case of the halides.



Depending upon the nature of the metal thus produced, it may further behave in one of the following manners:

- a. Undergo reduction to lower oxidation states.
- b. Catalyze the reaction between the alkali or alkaline earth metal and the solvent, which produces amides.
- c. React with the amide formed catalytically.
- d. Participate in no further reaction.

Although the reduction of negative ions has been studied only to a slight extent, the results obtained in these investigations indicate that the products may be either an ion of lower oxidation state i.e.,



or more than one negative ion.



The latter type of reaction is the one more frequently encountered in the studies to date.

In many instances, the reaction products have been established conclusively, although the isolation of these compounds has not been accomplished. A method of analysis based upon potentiometric titration has been of invaluable aid in obtaining the best information concerning the composition of these reaction products.

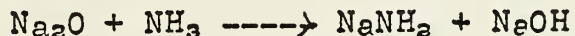
REACTIONS OF METAL-AMMONIA SOLUTIONS

A. Elements

Only a relatively small number of the elements react with solutions of metals in liquid ammonia. These include the normal members of groups IV, V, and VI of the periodic table. There is some evidence that finely divided transition elements, formed by the reduction of their compounds in liquid ammonia, react to a slight extent with metal ammonia-solutions.

In general, the elements react with these solutions to form a white or slightly colored ammonia-insoluble product corresponding to the normally stable oxidation state of the element (i.e. Na_2Se , Na_4Sn). In addition, most of these elements also form one or more ammonia-soluble salts containing homopolyatomic anions (Na_3Bi_3 , Na_4Pb_9), which impart intense characteristic colors to the solutions.

In the case of oxygen, the products formed are dependent upon the rate of addition of oxygen. In general, upon slow addition of oxygen, the alkali metal monoxide is first produced and is subsequently ammonolyzed e.g.



Further oxidation leads to the formation of the nitrite.

Rapid addition of oxygen to a solution of the alkali metals yields sodium peroxide, potassium peroxide and potassium dioxide. Potassium dioxide of 99% purity has been prepared at -50°C ., but at -53°C ., appreciable amounts of potassium nitrite and hydroxide are obtained. Attempts to prepare pure lithium peroxide have been unsuccessful.

B. Ammonium Salts

The simplest and most general reaction encountered in the study of solutions of metals in liquid ammonia is that of the ammonium salts: -



This reaction was one of the earliest studied and these investigations were initiated in an attempt to isolate the ammonium radical.

Ammonium salts are frequently used to eliminate excess alkali metal from a reaction mixture. On the other hand, ammonolytic reactions are brought to completion by the neutralization of the ammonium salts with alkali metals.

The hydrogen liberated upon the addition of a metal to a solution of an ammonium salt in liquid ammonia has been utilized in the in situ reduction of numerous organic substances. This procedure has been attempted in the case of inorganic materials, but the reaction does not differ from the one obtained in the absence of ammonium salts.

C. Hydrides

1. Ammonia

In general, the alkaline earth elements when dissolved in liquid ammonia react with the solvent to form definite molecular species of the type $\text{M}(\text{NH}_3)_6$, which may be isolated in definite crystalline form.

2. Hydrazine, phosphine and arsine

Hydrazine is almost entirely unreactive towards solutions of metals in liquid ammonia, however, phosphine and arsine usually react with these solutions to form dihydrogen phosphides and dihydrogen arsenides.

3. Water and the hydrides of sulfur and the halogens

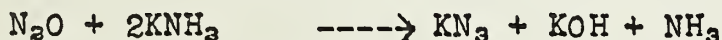
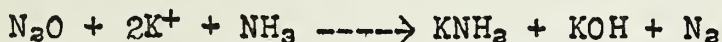
Water reacts with metal ammonia solutions as it does under ordinary conditions, while the hydrides of sulfur and the halogens form ammonium salts.

C. Oxides

In general, the oxides of the normal elements are reduced to the free element which, in turn, react with the excess alkali metal to form insoluble and/or soluble intermetallic compounds. The oxides of the transition elements are reduced to either a lower oxide or the free element, however, there is no subsequent formation of intermetallic compounds.

Liquid ammonia solutions of the alkali metals react with carbon monoxide to form carbonyls and with carbon dioxide to form salts of carbamic acid which are partially reduced to the formate by the hydrogen liberated in the course of the reaction.

Upon addition of nitrous oxide to metal ammonia solutions the amide is first produced which in turn reacts with more nitrous oxide to yield the azide.



Nitric oxide yields precipitates of nitrosyl compounds (NaNO , KNO) when added to these liquid ammonia solutions. Aqueous solutions of these nitrosyls give the characteristic silver salt of hyponitrous acid, but the x-ray diffraction pattern of sodium nitrosyl is different from that of sodium hyponitrite.

Nitrogen dioxide has not been thoroughly investigated, but is apparently reduced by a solution of barium to yield the same product as nitric oxide.

D. Sulfides

Sulfides usually react with solutions of the alkali metals in liquid ammonia to yield the alkali sulfides and intermetallic compounds (Na_3As_5 , Na_3Sb_7)

E. Halides and simple cyanides

The halides and simple cyanides are usually reduced to the free element in metal ammonia solutions. However, in the case of the transition elements, amide formation is appreciable as the free elements are excellent catalysts for amide formation.

In conclusion it should be emphasized that the reactions of inorganic substances in metal ammonia solutions have been studied to only a relatively small extent and the possibilities for further investigations in this field are essentially unlimited.

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PASSIVITY IN METALS

William Ulrich

November 7, 1950

Although the phenomenon of passivity has been recognized for over a century and a half, there remains a considerable amount of speculation as to its origin and nature. A number of theories have been proposed to account for this property, but most of them have been discarded or absorbed into other more extensive theories. Of the latter the Generalized Film Theory and the Electronic Configuration Theory appear to be of particular significance and will be discussed in the following sections.

Generally passivity is defined in two ways;

- 1) A metal active in the E.M.F. series, or an alloy composed of such metals, is considered passive when its electrochemical behavior becomes that of an appreciably less active metal.
- 2) A metal or alloy is passive if it substantially resists corrosion in an environment where thermodynamically there is a large free energy decrease associated with the passage from the metallic state to appropriate corrosion products.

For the most part passivity is restricted to the first definition in this discussion. This approximates the classical meaning as first presented by Schönbein and Faraday. Examples of passivity which may be considered under this definition include the behavior of iron, other transition metals, and passive alloys. On the other hand, the second definition includes such examples as the coatings on lead in sulfuric acid, on zinc in sodium silicate, and on silver in hydrochloric acid, as well as all those in definition (1).

The first recorded reference to passivity was provided by Keir (1), who observed that iron is not attacked by concentrated nitric acid. Wetzlar (2) continued the study and discovered that the property is not absolute, but may be shown in various degrees. In 1836 Schönbein (3) introduced the term "passivity" for the phenomenon.

Apparently Faraday (4) provided the first theoretical explanation, when he suggested that passivity is caused by a thin oxide film on the surface of the metal. This concept has been expanded into a more complete theory; namely the Generalized Film Theory mentioned above. At present, this is the most popular of all theories on the subject.

For a number of years this generalized picture was criticized, because in many examples the film appeared non-existent, as certain physical properties of the surface apparently were unaltered. This objection was largely discredited when Evans (5) actually succeeded in isolating the film from a metal specimen. Since then a number of films have been isolated and studied (6). The method involves the use of a strongly corrosive solution, as iodine in methanol, to attack the active metal under the film. Initial contact with this portion of the metal is obtained by scratching the surface. After the inner metal has dissolved, the film is removed, washed in methanol, and dried. Examination of the films may be made by spectrographic, colorimetric, and diffraction methods. Thus far, a number of stainless steels have been investigated and considerable evidence has been accumulated for the existence of iron and chromium in the passivating film. Mahla and Nielsen (6) suggest a spinel type of lattice, but other investigators dispute this view.

In the cases where oxide films are considered responsible for the passivating action, it appears that the M_2O_3 oxide is more effective than other types. This might be due to their insolubility. In the case of iron, ferric oxide is insoluble in many environments where ferrous oxide is soluble. Therefore, there is a possibility that an iron specimen will lose its passive condition if the ferric iron is reduced to the ferrous state. Such a reduction is favored whenever cracks form in the film; for the cell

Iron / Acid / Ferric Iron

is established. As the ferrous iron is formed, it moves away from the surface and thus leaves more iron exposed to the corrosive environment. On the basis of this argument it seems desirable to acquire thin films which would not be as likely to crack as less resilient thick films.

An even more striking example of the protective power of the sesquioxide than is shown in iron samples is found in the case of aluminum. Although this metal is very close to the reactive end of the Potential Series, a sample of high purity will withstand the corrosive action of hydrochloric acid, which is one of the most effective agents in destroying passivity.

It should be pointed out that substances other than oxide may form passivating films on metals. Langmuir (7) demonstrated that the film on specimens of passive tungsten is composed of molecular oxygen rather than a metal oxide. Likewise, adsorbed carbon monoxide on stainless steels forms a protective film that withstands the attack of hydrochloric acid.

One of the most interesting developments in this field has been the development of the "Electronic Configuration Theory" (8)(9)(10). Up to the time of its origination there had been very little to connect passivity to the nature of the metal itself. Instead the emphasis had been placed upon the environment. In this new theory, however, considerable attention is given to the electronic configuration of the metal atoms. Unfortunately the theory is restricted to transition elements only.

The theory assumes that the unfilled inner energy levels of the transition elements tend to fill with electrons in the same sense that is found for the outer levels in compound formation. A metal is considered active in the process of filling these vacancies, and passive when these levels are vacant. Thus, oxygen and oxidizing agents induce maximum passivity, because they tend to absorb electrons rather than donate them to the metal.

In the case of Fe-Cr Alloys (stainless steels), the chromium is believed to impart passivity to the iron by sharing at least one electron from the iron atom. On the basis of five vacancies in the d orbitals of chromium, it might be expected for one chromium atom to passify five iron atoms. This corresponds to 15.7% Cr by weight, whereas about 12% Cr is found necessary in practice.

As the theory was presented in 1939, very little significance was imparted to the surface atoms, but recently the theory has been modified to the extent that the ennobled potentials attained with passivity are thought to depend primarily on the surface metal atoms. If the electronic configuration of these permits reaction with the surrounding medium, a protective product may form on the surface. In this sense the theory is similar to the Generalized Film Theory. If no reaction occurs, there is the possibility that the medium may be adsorbed on the surface of the metal, and so satisfy secondary valence forces of the metal atoms near the surface.

The condition that determines whether a substance capable of reaction will react or adsorb appears to be connected to the work function ($w.f.$) of the metal (i.e., the heat of evaporation of electrons from the metal) and the heat of sublimation (ΔH_s) of the metal. For example, when oxygen approaches a metal surface, it will be adsorbed or else a metal atom will be dislodged from its position in the lattice to form an oxide. The preferred process is that requiring the lesser amount of energy. Thus, passivity results for the relation $\frac{w.f.}{\Delta H_s} < 1$ and activity for $\frac{w.f.}{\Delta H_s} > 1$. Therefore, alloying, which effects both $w.f.$ and ΔH_s , can induce passivity or activity depending upon the approximate ratio of quantities of the alloy composition.

The relative merits of this theory include;

- 1) The predictions of passivity of iron alloys are in fair agreement with experimental facts.
- 2) It relates electron configuration to the per cent of a metal which is necessary to promote passivity.
- 3) It offers a link between passivity and other properties of metals (as magnetic susceptibility).

The most obvious objections are;

- 1) The internal structure of the metal is assumed to be of far greater importance than the environment.
- 2) The authors based the theory on the study of a relatively few alloy systems. Other investigators have found discrepancies in the theory as applied to other systems.
- 3) It applies only to transition elements.

In order to clarify the statement of the first objection mentioned above, a brief discussion of the influence of the environment is in order. Oxidizing media generally enhance passivity. This is ascribed to the fact that these agents tend to absorb electrons rather than lose them. Reducing conditions, which may donate electrons to the metal atoms, tend to destroy passivity.

In general, halogen ions are very effective in the removal of the passive condition. It is suggested (9) that the breakdown is preceded by changes in the electronic configuration of surface metal atoms at local areas. This may be brought about by the effect of the intense electric fields of the halogen ions. In any event it is indicated that small nuclei of active metal are formed which in contact with the passive metal, produce a considerable potential difference and subsequent galvanic action.

Whenever the passive state is desired, certain compounds called passivators may be added to the bath. It has been found that chromates are particularly useful. A possible explanation for the action is provided by Evans (11), who assumes that the chromates react with one of the corrosion products of the metal. In the case of iron this may be a ferrous salt. If this is true, there is the possibility for the formation of a precipitate which contains Fe (III) , Cr (III) , OH^- , and CrO_4^{--} . Thus, when a trace of ferrous salt is produced at a discontinuity in the film, it produces a precipitate in physical contact with the surface, which acts to seal the discontinuity.

An alternative explanation for this action is given by the Electron Configuration Theory (10). It assumes that the chromate ions are absorbed on the surface of the metal. Here they share electrons from the surface iron atoms, but do not disrupt the metal lattice.

When one considers the tremendous cost and inconvenience of corrosion, the importance of passivity becomes clear. In this regard a continued study of the theory of passivators and the effect of electronic configurations which may bring about better corrosion resistant alloys seems highly desirable.

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ELEMENTS 97 and 98

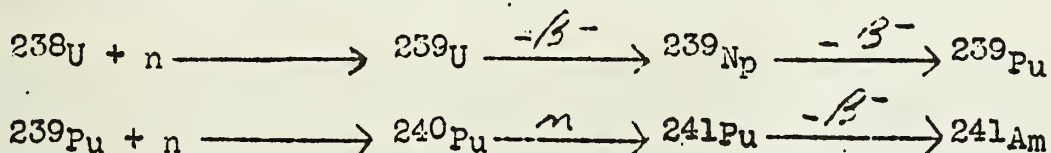
James W. Curry

November 14, 1950

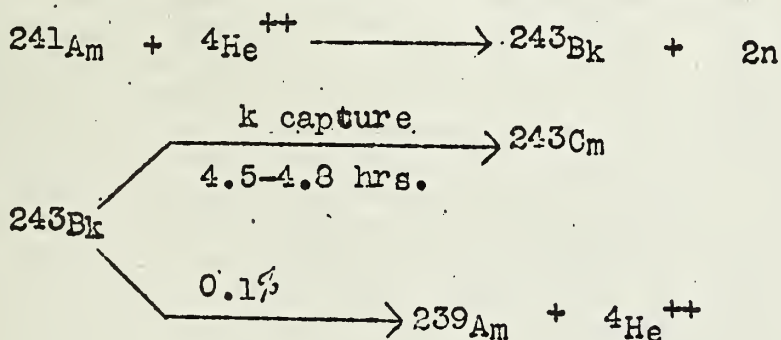
Synthesis

Within the past year have come announcements from G. T. Seaborg and his co-workers of the discovery of two transcurium elements. They reported that they had synthesized elements of atomic numbers 97 and 98 in the Berkeley 60 inch cyclotron.

The starting material was ^{238}U which was made to undergo a series of transformations outlined as follows (7):

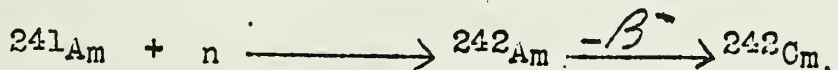


For the synthesis of element 97 (Berkelium, Bk), ^{241}Am was then bombarded with alpha particles. The particular isotope discovered was thought to be of mass 243 or possibly 244, decaying with a half-life of 4.5 to 4.8 hours by electron capture, with approximately 0.1% alpha decay branching (4,8,9):



There seem to be 3 alpha particle groups associated with the activity, the highest energy being about 6.72 M.e.v. (9).

^{242}Cm , made from ^{241}Am (7) according to the reaction,



was converted to an isotope of element 98 (Californium, Cf) by irradiation with 35 M.e.v. helium ions:



The isotope which was identified has an observed half-life of about 45 minutes and probably has the mass 244 as indicated (6, 7, 10). The observed mode of decay is through the emission of alpha particles with energy about 7.1 M.e.v. which agrees with predictions (6, 10).

Chemical Separation and Identification

Chemical separations and identifications have been carried out. The chemical separation of element 97 and other reaction

products from the target material was made by combinations of precipitation and ion exchange adsorption methods, making use of the anticipated III and IV oxidation states of berkelium and its position as a member of the actinide transition series. The separation involved oxidation of the americium formed in the bombardment by oxidation to the fluoride soluble VI state, precipitation of the insoluble fluorides using lanthanum fluoride as carrier, then removal of berkelium, curium and any unoxidized americium from the other products by adsorption of the dissolved mixture on Dowex 50 resin and selectively eluting them with 13 M HCl. Berkelium, curium and americium were then separated from one another by adsorption on Dowex 50 and elution with ammonium citrate (buffered with citric acid to pH 3.5) at a temperature of 87° (8, 9).

The first successful identification of element 98 depended on the quite accurate prediction of some of its nuclear and chemical properties. The anticipation of the nuclear properties (principally half-life and radiation characteristics) was necessary in order to design adequate chemical procedures of sufficiently short duration and to use suitable instruments for the detection of its radiations. The chemical procedure consisted essentially of dissolving the curium oxide target in 6 M HNO₃, adding 200 micrograms of La³⁺, and precipitating the lanthanum hydroxide with ammonium hydroxide. Lanthanum hydroxide carries the heavy actinides and many fission products. The hydroxide precipitate was dissolved in 0.5 M perchloric acid, adsorbed on a small amount of ammonium form Dowex 50 cation exchange resin, and placed on top of a column packed with the same resin. The eluting agent was ammonium citrate buffered with citric acid to a pH of 3.5 (total citrate concentration 0.25 M). In order to decrease the time of separation, the elution was carried out at an elevated temperature of 87°. In this elution experiment 7.1 M.e.v. alpha particles were found very close to the expected position of elution of element 98. These alpha particles decayed with a half-life of about 45 minutes. This single experiment probably offers sufficient evidence for the discovery of element 98 (6).

Chemical Properties

Berkelium has been found to be chemically related to terbium, although this had been predicted, since the element occupies a position in the actinide series analogous to that held by terbium in the lanthanide family. Seaborg had predicted a IV oxidation state and had considered in view of the lower binding energy of the 5f electrons as compared to the 4f electrons that it might be easier to oxidize element 97 to this IV state than it is in the case of terbium (6). Actually, berkelium is not only oxidizable to the IV state, but the oxidation can be carried out in aqueous solution, this being in marked contrast to terbium which can be oxidized to the IV state as solid TbO₂ only in the dry condition (3, 8). Table I shows the results of a series of carrying experiments in which solutions containing ²⁴³Bk tracer were treated with oxidizing agents of various strengths. Carrying with zirconium phosphate or cerium (IV) iodate was used as the test for oxidation, it being assumed that Bk(IV) would be carried and Bk(III) not carried by these precipitates. After the separation of the precipitate, a precipitation of lanthanum

fluoride was made from the supernatant in order to check the amount remaining there. It has been shown in many experiments that lanthanum fluoride carries Bk(III) fluoride quantitatively and, in fact, all indications point to similar behavior of Bk(III) to that of the tripositive actinide and lanthanide elements in other chemical properties. In the zirconium phosphate or cerium (IV) iodate experiments, carrying of some 90% of the berkelium is considered to represent essentially complete oxidation to the IV state, while carrying of some 5% is considered to represent no oxidation on the basis of analogy with the behavior of other actinide elements in tracer experiments (8).

Table I

Carrying of Tracer Berkelium from Solutions of Various Oxidizing and Reducing Strengths

Conditions for Oxidation	% Carried by Zirconium Phosphate
3 M HCl, reduced with Zn amalgam, 25°	5
3 M HCl, satd. Br ₂ , 75°, 15 min.	5
3 M HCl, satd. Cl ₂ , 75°, 15 min.	5
3 M HNO ₃ , 75° 15 min.	5
3 M HNO ₃ , 0.1 M NaBrO ₃ , 0.2 M H ₃ PO ₄ , 75°, 5 min.	85
7 M HNO ₃ , 0.1 M NaBrO ₃ , 25°, 15 min.	83
5 M HNO ₃ , 0.1 M Na ₂ Cr ₂ O ₇ , 75°, 15 min. heated 15 min. at 75° after pptn.	89
0.015 M Ce(IV), 0.015 M Ce(III), 8 M HNO ₃ , 75°, 5 min.	56 ^a
0.015 M Ce(IV), 0.006 M Ce(III), 3 M HNO ₃ , 75°, 5 min.	69
0.015 M Ce(IV), 8 M HNO ₃ , 75°, 5 min.	80

As seen in Table I, Bk(III) is oxidized to Bk(IV) by dichromate, bromate and cerium (IV), but not by nitrate nor by chlorine. The oxidation by bromate ion has been shown to be a function of the hydrogen ion concentration. This and other experiments indicate that the formal potential of the Bk(III) - Bk(IV) couple varies with its environment and is similar in that respect to the Ce(III) - Ce(IV) couple. The values for both are about -1.65 volts (4).

The results of experiments with californium have revealed only the tripositive oxidation state of eka-dysprosium character (7). Several attempts were made, using strong oxidizing agents, to oxidize Cf(III) to a higher oxidation state. Carrying on zirconium phosphate was used as a test for Cf(IV) on the basis of analogy with the behavior of other actinide elements in tracer experiments. Experiments performed after oxidation with 0.2 M ammonium persulfate for 10 minutes at 70° in a solution 1 M in nitric acid and 0.2 M in sulfate showed less than 10% carrying on zirconium phosphate and greater than 80% carrying on lanthanum fluoride precipitated by adding La³⁺ and making the supernatant 1 M in hydrofluoric acid. Similar experiments after oxidation with sodium bismuthate for 5 minutes at 60° in

^aCerium(IV) iodate used as carrier here and following experiments.

5 M HNO_3 also showed less than 10% carrying on zirconium phosphate and greater than 80% carrying on lanthanum fluoride from the supernatant made 3 M in hydrochloric acid and 1 M in hydrofluoric acid. Although there are uncertainties in the tracer experiments, due largely to the small amount of californium available, it can be concluded that the oxidation of $\text{Cr}(\text{III})$ to the IV or VI states in aqueous solution is not possible even with these strong oxidizing agents or that the oxidation is slow (6, 7). The difficulty of oxidizing berkelium to the IV state indicates that such higher oxidation states may not be expected. However, as the second element beyond the midpoint of this transition series, the possibility of oxidation to a V state (CrO_2^+) must be borne in mind, particularly in view of the great stabilizing influence of the two oxygen atoms found in these actinide elements for the MO_2^+ (and MO_2^{+2}) type of ions (6).

The chemical properties of berkelium and californium all indicate that they fit in well as the eighth and ninth actinide elements, respectively. Perhaps the best evidence for this is a comparison of the relative rates of elution by ammonium citrate of the actinide elements californium, berkelium, curium and americium, and their rare earth homologs dysprosium, terbium, gadolinium and europium. To facilitate this comparison, the elution data for the rare earths and the actinides are plotted together in Fig. 1.

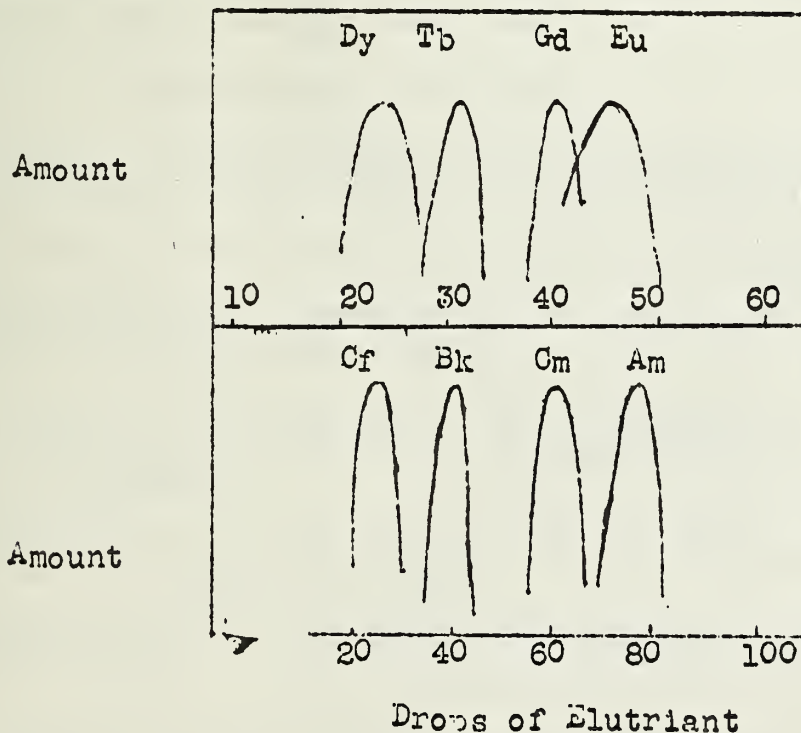


Fig. 1. Comparison of the rates of elution of californium, berkelium, curium and americium with their homologs dysprosium, terbium, gadolinium and europium.

Here the ordinates are normalized to show equal amounts of activity. A remarkable analogy between these two groups is apparent, indicating that the same sequence of changes in ionic radius is encountered on filling in the 5f electrons as occurs on filling the 4f shell. It seems quite clear that curium represents the midway point in the actinide transition series of elements. The most obvious difference between the two groups is the larger magnitude of the contraction found in the actinides. That this should be the case is quite reasonable when it is considered that the more loosely bound 5f electrons of the actinides would certainly be less effective as shielding electrons (6, 8).

Summary

The discoveries of elements 97 and 98 have provided further evidence for the existence of an actinide rare earth series. The actinide hypothesis was used to predict accurately the chemical properties and half-lives of the new elements and therefore was an invaluable aid in pointing the way to their discovery and in successfully utilizing chemical separation methods for them (1, 2).

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COBALT COMPLEXES of 1,2-DIPHENYLETHYLENEDIAMINE

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The possibilities of resolution of racemates on the basis of preferential coordination of one of the optical antipodes of a racemic mixture to the exclusion of the other has been demonstrated by the work of Jonassen (1), Johnson (2), Hamilton (3), and Sister Martinette (4).

Jonassen was able to effect a partial resolution of racemic tartaric acid into its optical antipodes on the basis of his experimental observation that of the two tartrato complexes, $[\text{Co } \underline{1\text{-pn}_2} \underline{\text{d-tart}}] \text{Cl}$ and $[\text{Co } \underline{1\text{-pn}_2} \underline{1\text{-tart}}] \text{Cl}$, the levo-tartrato complex reacted many times more rapidly than the dextro-tartrato complex with levo-propylenediamine to yield the tris-levo-propylenediamine cobalt(III) ion. Subsequent work by Hamilton further substantiated the validity of Jonassen's approach by demonstrating experimentally that dextro-tartaric acid replaced the coordinated tartrato group in the complex $[\text{Co } \underline{1\text{-pn}_2} \underline{1\text{-tart}}] \text{Cl}$. Johnson, in a modification of Jonassen's procedure but employing the same general principle of coordinative selectivity of optical antipodes, effected an almost 70% resolution of propylenediamine by employing the difference in reactivity existing between $[\text{Co } \underline{1\text{-pn}_2} \underline{\text{d-tart}}] \text{Cl}$ and $[\text{Co } \underline{\text{d-pn}_2} \underline{\text{d-tart}}] \text{Cl}$.

Inasmuch as it was clearly indicative that resolution of racemates on the basis of preferential coordination depends upon the asymmetry existing within the coordination sphere, it is reasonable to assume that an increase in asymmetry within the coordination sphere might further increase its selectivity toward one of the optical antipodes comprising a racemic mixture. To increase the asymmetry within the coordination sphere above and beyond that existing in the cobalt complexes of levo-propylenediamine requires a cobalt amine complex which contains a diamine characterized by the presence of two asymmetric centers instead of one. An investigation was therefore undertaken involving the coordination of a 1,2-diamine containing amino groups attached to adjacent carbon atoms. The particular amine chosen for this work was 1,2-diphenylethylenediamine. This amine contains two similar asymmetric carbon atoms and exists in meso and racemic modifications.

Since 1,2-diphenylethylenediamine is not commercially available, it was necessary to find a convenient method for its synthesis. Of the several different methods reported in the literature for the synthesis of this amine, the one reported by Lifschitz (4) appeared to be the most promising. It was found, however, that several modifications of Lifschitz's procedure were necessary to prepare the amine in good yield by a convenient procedure. Several modifications of Lifschitz's procedure were made and in general the procedure was improved to the extent that the amine can now be prepared in the laboratory on a relatively large scale and in good yields. The synthesis as modified involves the condensation of benzaldehyde with liquid ammonia to yield hydrobenzamide which is subsequently rearranged to amarine by heating at 120°C. The

amarine so produced is in turn rearranged to isoamarine by heating at 160°C in diethyleneglycol containing dissolved sodium hydroxide. Isoamarine is acetylated and the acetyl derivative is subsequently hydrolyzed to yield racemic-N-acetyl-N'-benzoyl 1,2-diphenylethylenediamine. Hydrolysis of the diacyl derivative in a solution of glacial acetic acid yields the amine dihydrobromide from which the free amine is obtained by treatment with a solution of sodium hydroxide. The meso form of 1,2-diphenylethylenediamine is obtained in a similar manner except, that amarine is acetylated and subsequently hydrolyzed to the amine.

The coordination complexes of 1,2-diphenylethylenediamine with cobalt are in general much less soluble in water and much more soluble in polar organic solvents than the corresponding cobalt complexes of propylenediamine and ethylenediamine. Evidence obtained to date indicates that in general the complexes containing the meso amine are less stable and more difficult to prepare than those of the racemic base. Whereas the trans-dichloro-bis-1,2-diphenylethylenediamine cobalt(III) chloride containing the racemic amine is quite stable and easy to prepare, the corresponding complex containing the meso amine is not very stable and is difficult to prepare. Another indication of the relative stability of the complexes containing the racemic amine as compared to the instability of those containing the meso amine is indicated by the fact that the tris-1,2-diphenylethylenediamine cobalt(III) chloride containing the racemic amine is quite stable and easy to prepare whereas attempts to prepare the tris- complex of the meso amine have been unsuccessful.

Trans-dichloro-bis-1,2-diphenylethylenediamine cobalt(III) chloride of the racemic base may be prepared in good yields by hydrogen peroxide oxidation of an alcohol solution of cobaltous chloride and the amine. The trans-dichloro complex is insoluble in water at room temperature but dissolves slowly in boiling water as the aquated complex. Upon concentration of a solution of the aquated complex, the unaquated trans-dichloro chloride complex crystallizes indicating that the aquated complex is unstable. Attempts to prepare the cis-dichloro chloride complex by heating and evaporation procedures as employed in preparing the corresponding cis-dichloro complexes of propylenediamine and ethylenediamine have been unsuccessful.

To undertake resolution studies similar to those reported using propylenediamine complexes of cobalt, it was necessary to develop a synthesis for carbonato and tartrato complexes of cobalt containing 1,2-diphenylethylenediamine. Attempts so far to prepare the carbonato-bis-1,2-diphenylethylenediamine cobalt(III) complex have resulted in the synthesis of aquo or diaquo carbonates which appear to decompose rather than lose their aquated water. Similarly, attempts to prepare tartrato-bis-1,2-diphenylethylenediamine cobalt(III) complex have resulted in aquated complexes which like the carbonato appear to decompose before losing aquated water.

Inasmuch as attempts to prepare the tartrato complex have been unsuccessful, there has been no experimental verification of the original assumption that the presence of greater asymmetry

within the coordination sphere will effect a more pronounced selectivity in the coordination of one optical antipode to the exclusion of the other. Furthermore, on the basis of the experimental data obtained, it appears unlikely that a stable tartrato complex will be isolated since the condition of stability of the 1,2-diphenylethylenediamine complexes seems to be tied up very definitely with considerations of symmetry of the complex ion. As evidence to substantiate the claim that maximum symmetry is the prerequisite for maximum stability of these complexes attention may be focused on a generalization based on experimental evidence that attempts to prepare unsymmetrically substituted cobalt complexes of 1,2-diphenylethylenediamine have been as yet unsuccessful.

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ULTRASONIC WAVES IN THE OXIDATION
OF POTASSIUM IODIDE SOLUTION

Donald Beeson

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The chemical effects of ultrasonic waves have been investigated by a great many workers and in connection with a large variety of chemical reactions. One of the most frequently investigated reactions has been the oxidation of potassium iodide solution with the subsequent liberation of iodine.

Schmitt, Johnson, and Olson (1) showed that iodine is produced when ultrasound travels through potassium iodide solution containing dissolved air. They believed that this was the result of the formation of hydrogen peroxide from the dissolved oxygen which was activated by cavitation. Liu and Wu (2) agreed that both oxygen and cavitation were necessary and also found that the addition of carbon tetrachloride to the solution greatly increased the yield of iodine. They postulated that the carbon tetrachloride reacted with the activated oxygen to give free chlorine which then oxidized the potassium iodide.

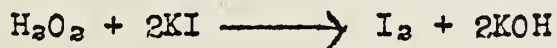
Many other workers have studied this reaction and a variety of results has been obtained. In this and in other reactions involving ultrasound it has been found very difficult to reproduce results quantitatively. In the article which is being reviewed in this seminar, Weissler, Cooper, and Snyder (3) have attempted to control as many of the variables as possible among those involved in ultrasound work and to elucidate the nature of this reaction.

The apparatus used here was the ultrasonicator which provides electrical energy up to 600 watts at frequencies of 400, 700, 1000, and 1500 kilocycles, which can be fed to a quartz crystal immersed in transformer oil. The reaction vessel is clamped in place in the oil a few centimeters above the crystal.

The energy in an ultrasonic wave is carried through the medium by the back and forth motion of the molecules, which produces alternate compressions and rarefactions. There are considerable alternations of pressure between compression and tension at a given point in the liquid and these large pressure changes result in cavitation - that is, the formation and violent collapse of small bubbles or voids in the liquid.

In the work carried out by these investigators, the liberation of iodine from potassium iodide solution was studied both in the presence and the absence of carbon tetrachloride.

If, in the absence of carbon tetrachloride, the oxidation is caused by ultrasonically-produced hydrogen peroxide, equivalent quantities of free iodine and hydroxyl ion should be formed, as:



This was verified experimentally by continuous titration with both sodium thiosulfate and hydrochloric acid.

It was found that the rate of iodine liberation when the potassium iodide solution was half-saturated with carbon tetrachloride at the start was five times as great as that of a solution containing no carbon tetrachloride. The rate of a fully-saturated solution was fifteen times as great as that of the solution containing no carbon tetrachloride.

Since it has been difficult to obtain reproducible results, attempts were made to evaluate the effects of some of the experimental variables involved. Glass test tubes were used as reaction vessels and after trying ten different sizes of test tubes, it was found that the yield of iodine was not a function of the test tube diameter. However, the yield did appear to be a periodic function of wall thickness of the test tubes, related to the fact that sound energy passing through a barrier is a maximum when the thickness corresponds to an integral number of half wave lengths.

It was also found that it was necessary to position the test tube very accurately above the crystal and to clamp it tightly. By careful control of all these factors it was possible to reproduce results within 5 or 10%.

It was found that with a 5 minute radiation at constant power input, increasing the volume of potassium iodide solution caused a rapid increase in yield up to a certain point and then a gradual falling off at still larger volumes. This indicates that there is an optimum ratio of ultrasonic power to volume of liquid.

It was found that the yield of iodine is almost independent of potassium iodide concentration except for very dilute solutions, where the yield drops off. This would indicate that as long as there is enough potassium iodide present to react with all of the oxidizing agent, it doesn't matter how much additional potassium iodide is present.

Increasing the frequency from 400 to 1500 kilocycles while keeping the power input constant caused an irregular variation in iodine yield due to varying transparency of the test tube to ultrasonic energy of different frequencies.

If all other factors were held constant and the power input increased, the yield for a 5 minute irradiation increased almost linearly if the volume of the solution was 200 ml. or larger. However, for smaller volumes the yield first increased and then decreased sharply.

It was observed that when potassium iodide solutions containing carbon tetrachloride were saturated with helium, the yield of iodine was as great as that from air or oxygen saturated solutions. This shows that the free chlorine is not liberated from carbon tetrachloride by activated oxygen or a similar oxidant,

as there is no reaction between helium and water which could produce such an oxidant. Instead, the carbon tetrachloride itself is probably involved in the primary sonochemical reaction, the carbon to chlorine bond being broken by the large mechanical forces generated at the collapse of cavitation bubbles. In order to facilitate cavitation, some dissolved gas should be present, but it need not be oxygen.

In order to learn something of the mechanism of the reaction of carbon tetrachloride, solutions containing known amounts of carbon tetrachloride were irradiated until the rate of iodine production decreased to the point where it was judged that all the carbon tetrachloride had reacted. It was found that very close to 4 atoms of oxidizing chlorine were obtained from each molecule of carbon tetrachloride. Since the other reactant (water) was present in large excess, it was thought that the reaction might be first order. This postulate was strengthened when it was found that the half life of the reaction was independent of the initial concentration. However, another criteria for a first order reaction is that the log of concentration of unreacted material plotted against time give a straight line. Here there is an initial sharp drop before a straight line is obtained. This could be the result of two consecutive first order reactions, the first being more rapid than the second and each producing two oxidizing chlorines per molecule. On this basis a theoretical rate was calculated and found to agree pretty well with the observed results. The tentative proposal made for the chemical nature of these two consecutive reactions is:



Some of the evidence in favor of this proposal is as follows: the second reaction is found to occur independently when a hydrochloric acid solution was irradiated. Also by adding excess alkali to the solution to prevent the second reaction, only one-half as much chlorine was obtained as before. Another point is that the first reaction creates hydrochloric acid while the second destroys it. This checked with the results as the acidity was found to increase at first and then decrease (the first reaction being nearly complete in 10 minutes).

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The Organic Compounds of Tin and Other Fourth Group Elements

M. M. Robison

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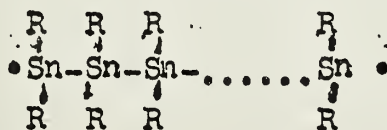
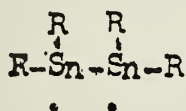
General -- The organic compounds of group IV b serve well to illustrate the gradual change in properties of elements in the group, such as decreasing strengths of M-M, M-C, and M-H bonds, and increasing electropositivity. The transition in the organic chemistry is most marked between germanium and tin, and this abrupt change is consistent with the chemistry of the free elements and their inorganic compounds. Indeed, the chemistry of organo-germanium compounds is fairly representative of organo-silicon chemistry, while that of the tin analogs closely corresponds to that of lead.

Organic Compounds of Stannous Tin -- Stannous dialkyls and diaryls represent the first examples of formation of isolable, well-characterized divalent organic compounds by an element of the fourth group.

The most important methods of preparation include action of an alkyl halide on tin-sodium alloy, reduction of a dialkyl tin dihalide with zinc, and, probably most useful, reaction of a Grignard Reagent with stannous chloride.

The dialkyl compounds, low-melting oils which can be neither distilled nor recrystallized, have probably never been obtained in a pure state. Diaryls are much easier to handle, being solids, often with definite melting points. They are yellow powders, which form red solutions in benzene. Cryoscopic measurements in this solvent indicate that the aryl compounds are monomeric when freshly prepared, but that they polymerize after a few days approximately to the pentameric state.

In an effort to determine whether the monomers exist as biradicals, and to demonstrate the structure of the polymers, Jensen (1) has recently studied the magnetic susceptibility and dipole moment of tin diphenyl. He found that the material has a small dipole moment (about 1.10 D.), and that it is definitely diamagnetic. He further observed that the dipole moment is not affected by the degree of aggregation of the material. On the basis of these factors, as well as the color, he assigned the following structures to the polymers, and concluded that the electrons shown here and in the monomers are at all times coupled.



Several objections suggest themselves. In the first formula, if the electrons are indeed coupled they constitute an ordinary covalent bond, and the dipole moment of the resulting structure should be zero. In the second formula it is difficult to see why two so widely separated electrons should at all times remain coupled, and also why the resulting structure should in any case have a dipole moment. There would probably be free rotation about the bonds, and the author realized this, but nevertheless concluded that the resulting structure would have a moment n times that of the monomer, where n is the number of tin atoms in the chain. The polymerization only to a pentamer, furthermore, seems suspiciously coincidental, when one considers that saturated chains of tetrahedral atoms naturally assume a ring configuration. If a pentamer were built up either as Jensen postulates, or by a series of coordinate covalent bonds, it is difficult to see why a ring would not be formed.

The most important chemical characteristic of the stannous compounds is their extreme tendency to oxidation. Thus all of them on exposure to air add oxygen more or less rapidly; the tendency to addition decreases as the size of the substituent groups increases. They also add halogens and alkyl halides, and disproportionate on heating or attempted distillation (inert atmosphere) to form the tetrasubstituted compound and elemental tin.

Stannic Alkyls and Aryls

Monostannanes -- The most useful methods for the preparation of symmetrical monostannanes include reaction of Grignard Reagents, and Zinc and lithium alkyls and aryls with stannic chloride (2,3,4). Since substitution always occurs in a stepwise manner, an excess of alkylating agent must be employed.

Unsymmetrical compounds, containing either mixed alkyl aryl or mixed groups of the same type, are prepared by the obvious methods of allowing mono- or dihalides to react with the above reagents.

Tetraalkyl tin compounds are colorless liquids, stable to air and water. Tetraaryls are solids. The materials neither polymerize nor coordinate, and unsymmetrical compounds, although more active than the symmetrical, as is generally the case with organo-metals, show no tendency to disproportionate.

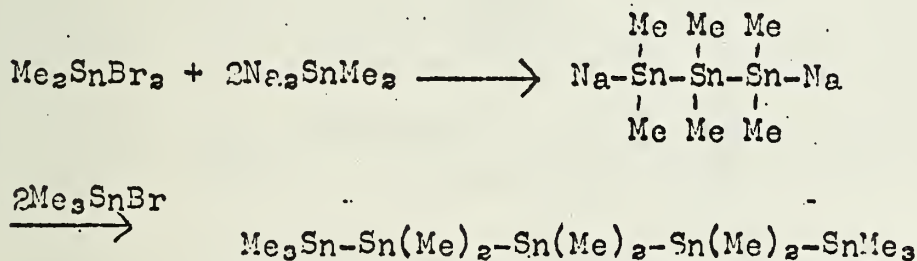
The materials are subject to cleavage by hydrochloric acid (5) and halogens; the decreased stability of the tin-carbon bond as compared to the germanium-carbon linkage is indicated qualitatively by the fact that chlorine and bromine tend to strip off two groups, while with the corresponding germanium compounds only one is removed. According to Manulkin (6) the smaller or more highly branched alkyl groups are removed from mixed alkyl compounds, while alkyl groups are held more firmly than aryl.

Distannanes -- Hexaalkyl distannanes are best prepared by the action of sodium on trialkyl halides in liquid ammonia. The liquid products may then be purified by distillation in an inert atmosphere. They are powerful reducing agents, and unlike the corresponding hexaaryl compounds are rapidly oxidized by air to form ether-like structures. All distannanes are cleaved by halogens, and also react with sulfur.

A comparison of degrees of dissociation of these compounds of the group IV b elements would be of interest, but the situation with tin is obscure. Cryoscopic measurements on hexamethyl distannane indicate that at least in dilute benzene solution it is almost completely dissociated into trimethyl tin (7), while vapor density measurements at 225° with the hexaethyl compound show no dissociation. (3). Magnetic susceptibility measurements, furthermore, are in disagreement with the first result, in that they show the hexamethyl compound to be diamagnetic in solution (9). Sidgwick concludes that in the solid colorless form the hexaryll compounds are probably undissociated, and that the same is probably true in the case of concentrated solutions. In dilute media, however, evidence seems to favor dissociation, as in the case of lead. It may be noted that silicon and germanium compounds of this type do not dissociate under any conditions.

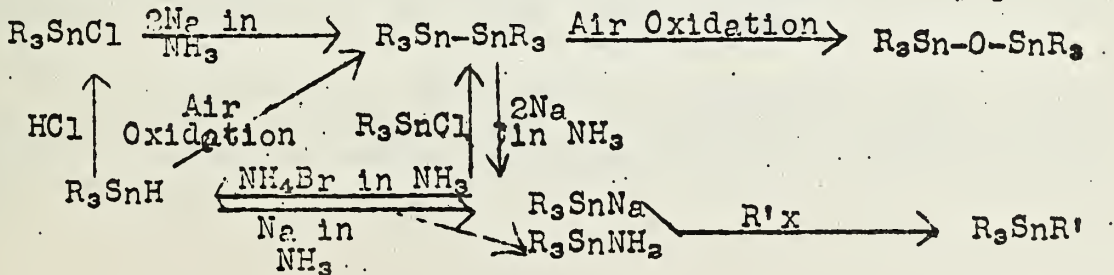
The hexaryl compounds are readily converted to the corresponding stanhol by such powerful oxidizing agents as potassium permanganate. (5).

Polystannanes -- The longest tin chain known at this time is one containing five atoms, with all other valences filled by methyl groups. It was prepared as follows (10).

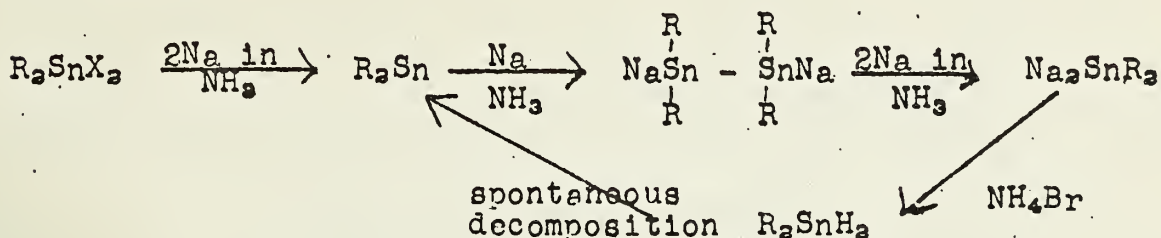


The product is a colorless oil, monomeric in benzene.

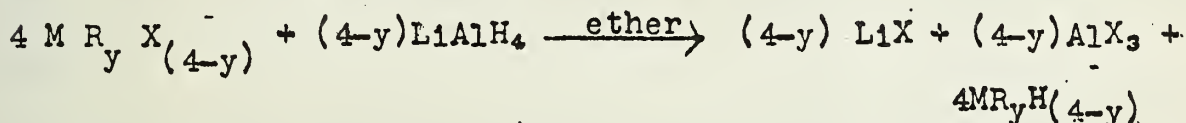
Hydrides -- Organo-tin hydrides have been prepared with one to three hydrogen atoms. Their manifold relationships to other compounds are seen in the following equations.



The dihydrides are not as stable as the monohydrides, and often decompose into the corresponding organo-stannous compounds. Intermediate stages of reduction have been demonstrated as follows (10).

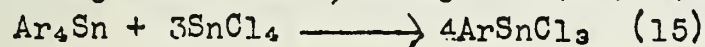
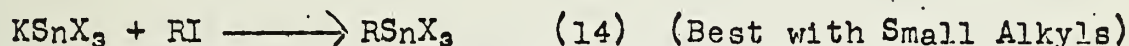
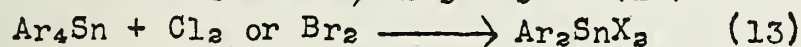
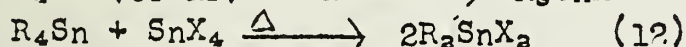


A trihydride has only recently been prepared by Finholt (11) using lithium aluminum hydride. This reagent has largely supplanted all others for the preparation of group IV hydrides, and the authors proposed a general equation.



Organo-Tin Halides

These compounds are known with one to three halogen atoms. Many methods of preparation are known for each class. Some of the best for the chlorides, bromides, and iodides are selected here.



These substances are all liquids or low-melting solids, soluble only in non-polar solvents. Like the lead compounds, and unlike their silicon and germanium analogs, they are only partially hydrolyzed by water. It is notable that these halides, unlike the hydrocarbons, have a coordination number of six. Werner (16) first found that the trialkyl monohalides, (which are not ammonolysed like the silicon and germanium compounds), form complex amines of the type $R_3SnX \cdot 2NH_3$.

The trihalides are hydrolyzed to stannonic acids. Either starting material or product may be converted by hydrochloric acid into the corresponding pentahalostannonic acids, of which salts are known.

In marked contrast are the properties of the fluorides. While silicon and germanium fluorides are similar to but more volatile than the chlorides, the tin and lead compounds show definite ionic character. The tin compounds are characterized by high melting points, solubility in water, and insolubility in organic media. They are prepared by precipitation from alcohol by action of potassium fluoride on another halide. With excess reagent complex salts of the type $K_2(R_2SnF_4)$ are formed.

Oxygen-Containing Compounds

Stannols, unlike silicols, (germanols are rare), show little resemblance to alcohols. They are, rather, crystalline solids with basic properties. On heating, the aryl compounds dehydrate to ether-like dimers, while the alkyls disproportionate. The monols are not very soluble in water, but have basic dissociation constants on the order of 10^{-5} . They form a series of ionic salts such as sulfates and nitrates, and covalent salts of carboxylic acids.

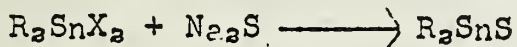
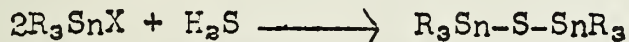
The chief method of preparation of both monols and diols is treatment of the corresponding halide with strong base.

The only true diols known are those with tertiary alkyl groups. Thus di-t-butyl tin dihydroxide, a solid, is feebly basic to litmus and soluble in non-polar solvents. Other diols dehydrate to form ketone-like structures, but these, like their silicon and germanium analogs, are actually highly polymerized amorphous solids. The diols also form a series of ionic salts.

No triols are known; the dehydrated stannonic acids, analogous in formula to carboxylic acids, are again highly polymerized amorphous materials which may be obtained either from an alkyl halide and sodium stannite, or by hydrolysis of trihalides. They are insoluble in organic solvents and water, but soluble in strong bases from which they are expelled by carbon dioxide.

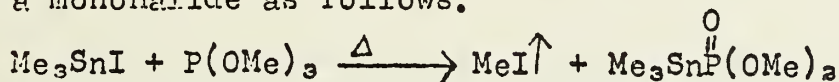
Other Elements

The corresponding oxidation states with sulfur have been prepared as follows (17,18)



The first product is a liquid, soluble in organic solvents, which reacts with hydrochloric acid with evolution of hydrogen sulfide. Cryoscopic measurements have shown the second to be a trimer, which, the author postulates, is a six-membered ring.

The most recent work in the field of organo-tin compounds is that of Arbuzov (19,20,21), who has prepared a series of compounds containing phosphorus. Thus trimethyl phosphite reacts with a monohalide as follows.



Analogous reactions have been run with phenyl phosphonic esters, and with dihalides of tin to form the double compounds. The author stated that all products were stable to water, but hydrolysed by acid.

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MERCURY IN CHEMICAL METALLURGY

Frank A. J. Moss

November 28, 1950

Introduction

Amalgam Metallurgy is the name applied to certain new processes developed in Germany during recent years, and apart from a few patents the work is relatively unknown. Several pilot plants are now in operation, as well as a full-scale plant for the extraction of zinc from roasted pyrites.

The amalgam processes replace coarse high temperature reactions by exactly controllable reactions in the cold, utilizing very dilute amalgams that are reactive and liquid at ordinary temperatures. They enable low grade ores to be used, giving a direct yield of pure metals as the end-products.

It is characteristic of the amalgam processes that the highest purity metal is obtained from grossly impure salt solutions in one stage, without additional purification. Alloys are more applicable, have a higher market value than the individual metals, and by the amalgam technique they can be prepared directly from the ore, without isolation of the individual metals. The finished products can be obtained either in solid or powdered form.

The Affinity of Metals for Mercury

Amalgams can be divided into three groups: the iron type, useful for the production of alloy powders; the zinc type, used for the preparation of pure metals; and the sodium type, which are useful for working up solutions that are difficult to electrolyze. This division corresponds to three degrees of affinity of the metals for mercury. The sodium type metals show the greatest affinity, form stoichiometric compounds, and react with considerable evolution of energy, whereas the zinc type metals have medium affinity and form mixed crystals. The iron type metals are generally not miscible with mercury and show only a slight affinity, the metals being attacked in the nascent state. Some other metals are not miscible with mercury.

Electric potential values can be used to characterize quantitatively the affinity of metals for mercury, but thermal data cannot be used directly. The melting points of the metals also play a part, with exceptions, in the division into amalgam types. The sodium type metals have the lowest melting points, and the iron type metals the highest melting points. Those metals which do not form amalgams have very high melting points, but gallium is an exception in being completely immiscible with mercury.

The Solubility of Metals in Mercury

The amalgam technique is concerned with easily flowing amalgams; either true solutions or very dilute amalgam sludges. The metals are handled in the flowing state in the cold.

Since mercury is opaque and metal suspensions can be very fine grained, and even colloidal, it is not always easy to recognize the heterogeneous nature of a dilute suspension, and therefore the literature contains widely varying values for the solubility of many metals in mercury. The fineness of a metallic suspension in mercury depends on the suspended metal and the mode of preparation. If the mercury is stirred during the electrolysis, particularly by superanics, fluid amalgams with quite high metal content can be obtained.

The highest solubility is shown generally by the metals of the zinc type; thallium having the highest value of over 40% at room temperature. Metals of the sodium type have slightly lower solubilities. The solubility of a metal in mercury always increases with increase of temperature, and for the very soluble zinc type this temperature effect is large. It is interesting to note that the metals having a high solubility in mercury occupy places next to mercury (both horizontally and vertically) in the periodic table; indicating a correlation between miscibility and the structure of the outer electron shells.

As is the case with aqueous systems, the soluble and insoluble components can be separated by filtration and sedimentation. The precipitates do not sink, but float on the mercury surface, and therefore filtration can be used for separating different groups of metals. Filtered amalgams are always free from metals of the iron type.

Metals dissolved in mercury are very reactive, and can easily be exchanged between mercury and an aqueous phase, whereas metals that are not easily soluble are unreactive and cannot be exchanged. Exchange between mercury and an aqueous phase plays an important part in the direct preparation of pure metals, and therefore insoluble metals of the iron type cannot be prepared directly in the pure state.

Metallic suspensions in mercury are often able to combine with a soluble component in the amalgam, even at room temperature, and precipitate an alloy (cold alloying), but cold alloying does not always occur between an insoluble and soluble component. Also only a fractional amount of the insoluble component is required to precipitate the whole of the soluble component. Easily soluble metals coming into contact in mercury generally produce a mutual increase in solubility.

Electric Potential Properties of Amalgams.

In all reactions of amalgams with aqueous solutions the potential difference at the mercury-water interface is of prime importance. For a dilute amalgam the solution pressure of the metal dissolved in the mercury is proportional to its concentration, and the amalgam potential is given by the Nernst equation.

The polarographic half wave potentials, which are independent of concentration, are an exact measure of the extent to which an amalgam of a given metal is electro-positive or negative with respect to another metal. With the aid of their

normal and half wave potentials amalgams can be arranged into an electromotive series. The zinc type amalgams have almost equal normal and half wave potentials, whereas the half wave potentials are more positive for the sodium type amalgams and more negative for the iron type amalgams, than their corresponding normal potentials. The amalgam potentials of the zinc and sodium types are reversible, but for the iron type amalgams the potential of formation is considerably more negative than the decomposition potential.

Three natural laws, having wide application in amalgam metallurgical techniques, can be derived from the electrode potential properties of dilute amalgams.

1. The potential of an amalgam is determined solely by its least noble component.
2. Since each amalgam strives to attain a more positive potential, those reactions which produce a more positive potential proceed spontaneously.
3. An amalgam cannot take part in a reaction which does not change its potential.

The potential of an amalgam is very sensitive to the presence of traces of less noble impurities, and therefore these traces of impurities can be rapidly removed by a phase exchange reaction. Phase exchange reactions can be applied to the separation of multi-component amalgams or salt solutions. The former are treated with an aqueous solution of a salt of the most noble component in the amalgam, and the latter with an amalgam of the least noble component. The prevailing amalgam potential can be used to operate electrical relay systems which will control the amount of salt solution and amalgam used for the extraction. Generally the salt solution and amalgam flow in counter current, enabling continuous separations to be made.

Surface Tension of Amalgams.

Molten metals have the highest surface tension of all liquids and therefore one would expect mercury to be a powerful adsorbent with high adhesion. (The surface tension of mercury is six times that of water.) The power of adsorption is shown by the fact that in alkali chloride electrolysis the mercury that is siphoned out of the cells carries with it adsorbed sodium chloride, on the other hand, mercury is known to wet only very few substances.

It has been known for many years that the surface tension of mercury changes considerably with its electric potential. Thus if two points in the same mercury surface are at different potentials, the mercury will flow from the point at the lower to the point at the higher potential, producing surface eddies which can be utilized in increasing the reaction rate at the boundary surface of phase exchange reactions, or in stirring metallic systems. This difference in potential can arise from

non parallel electrodes, or if there is a difference in current load due to one electrode being too small, or in phase exchange reactions where only part of the mercury surface is brought into the reaction.

Protective films on metallic surfaces can prevent amalgam formation, and it is for this reason that a polished iron surface cannot be coated with mercury. However, if the mercury contains a trace of sodium amalgam the protective oxide coating is reduced and amalgamation occurs at once. The amalgamation is not due to the lower surface tension of sodium amalgam, as it is known that iron will amalgamate with mercury if the former is in the nascent state. For similar reasons, zinc rod, but not zinc dust, can be amalgamated with pure mercury.

Special Properties of Amalgams

Free flowing amalgams are highly sensitive to oxidation, a mixture of the metal and oxide being formed when the amalgams are allowed to stand in air. It is possible to work with amalgams in the open air if they are covered with a solution which is able to dissolve the oxide film of the least noble metal component in the amalgam. Usually these oxide solvents will not attack the amalgam. For instance, very dilute hydrochloric acid or an ammoniacal solution of an ammonium salt can be used as an oxide solvent for zinc amalgam.

The high resistance of amalgams to attack by strong acids is said to arise from the high overvoltage shown by hydrogen at a mercury cathode. If the half wave potentials of amalgams are compared with the reduction potentials of various oxidizing agents at different pH values, it can be seen which amalgams will be attacked by a given reagent. Only when the potential of the given amalgam is more positive than the relevant reduction potential will reaction take place.

For the sodium and zinc type amalgams thermal decomposition takes place as a wet distillation, with the mercury boiling out of the liquid phase and the whole mixture melted. Solid ingots of metal are left after distillation. Dry evaporation occurs on distillation of the iron type and most alloy amalgams, and residues of powdered metal are produced.

The metals of the sodium and zinc types are not usually obtained by simple distillation due to the high affinity of the former for the mercury, and the relatively high temperatures (up to 900°C.) required to free the latter type from mercury. The iron type metals can be obtained easily, free from mercury, at relatively low temperatures.

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INORGANIC POLYMERIZATION REACTIONS

Earle Scott

December 5, 1950

Although polymerization is generally considered to be an organic phenomenon, there are several well known cases of inorganic polymerization reactions. As in organic chemistry, these processes may occur with or without the elimination of small molecules such as water. For the purposes of this discussion, the best known of these processes have been classified arbitrarily under the following headings.

1. Dehydration polymerization in solution
 - a) Anionic Aggregation--The formation of polyanions by dehydration of other protonated anions. Dependent upon $[H^+]$.
 - b) Cationic Aggregation--The formation of polycations by dehydration, brought about by the hydroxyl ion.
2. Condensation polymerization at elevated temperatures
 - a) Anionic Aggregation--A dehydration polymerization to yield larger anions. Induced by presence of acid materials, i.e. the proton donors or Lewis acids.
 - b) Cationic Aggregation--Formation of basic salts from hydrated salts by elimination of water and acid.
3. Molecular polymerization--Cases in which a molecule is the repeating link in the polymeric product. The exact mechanism of polymerization is not understood and may be different in each of the following examples.
 - a) Sulfur trioxide
 - b) Sulfur
 - c) PnX_2 ($X = Cl, F, OAr, HNR$ or NR_2)
4. Disproportionation polymerization as applied to polyphosphate systems.

Anionic Aggregation in Solution 10,13,20

The formation of polyanions is essentially a neutralization reaction in which hydrogen ions are attached to an anion and water is subsequently split out. In these processes water is sometimes lost intramolecularly and sometimes splits out intermolecularly to yield larger aggregates. That water is lost is apparent from the nature of the isolated products and the consumption of protons in the reaction, but this does not elucidate the mechanism of the reaction. The only evidence available to indicate the nature of these reactions has been presented by Jander and his coworkers based upon the following types of experiments.

1) Determination of diffusion coefficients for the anions of Mo^{6+} , W^{6+} , Sn^{4+} , V^{5+} , etc. at various hydrogen ion concentrations. It is assumed that ions obey the laws of diffusion as expressed by the equation

$$D \cdot n = \frac{k}{\sqrt{M}}$$

$$\frac{D_1}{D_2} = \frac{n \sqrt{M_2}}{n \sqrt{M_1}}$$

Where

n = viscosity
 M = ionic molecular Weight.

A standard (dichromate) is employed to establish D_1 under a given set of experimental conditions; other anions are then compared with it. The measurements are subject to rather wide fluctuations but serve to indicate the degree of aggregation quite well in many cases. The variations may well be due to mechanical difficulties as well as to field effects and to the hydration of the anions.

These measurements indicate that there is a great deal of variation in the aggregation patterns of the materials used. Molybdates show a clear cut stepwise aggregation from MoO_4^{2-} ions to ions containing 3, 6, 9, 12 and 24 molybdenum atoms. Such a polymerization could be accounted for by interionic dehydration. Tungsten, on the other hand, shows only two stable anions, i.e. WO_4^{2-} and $[\text{W}_6\text{O}_{21}]^{6-}$. The transition occurs over a range of 2 pH units and it is probable that intermediates exist but no one ionic species is sufficiently stable to give a diffusion coefficient. Aggregation in the vanadate system is again different, since evidence is obtained for ions containing 2, 4, and 5 vanadium atoms. The problem of the transition from a V_4 aggregate to a V_5 aggregate is unexplained. It is also reported that the vanadium exists in an anionic state on the acid side of the isoelectric point. No individual ionic species can be identified in the stannate system by a study of the diffusion coefficients. The diffusion coefficient drops along a smooth curve indicating gradual or continuous, rather than stepwise aggregation.

Dialysis experiments have also been carried out to demonstrate the presence of more than one ionic species at a given pH, assuming that two such species would give a diffusion coefficient which would vary with time. Because of the difficulties involved in reproducing membranes, these data are not subject to statistical treatment.

While the results of such diffusion experiments have aided in clarifying the picture of anionic aggregation the method is subject to some severe limitations. Analogies between various anions can be drawn only in very general terms. Ionic weights can not be determined accurately. The calculated values may vary 10% from the theoretical ionic weight assigned to the ion. Ions existing in solution, according to Jander's work, do not, in all cases, correspond with the composition of the material isolated from such a solution. Changes in the degree of aggre-

gation, occurring during the isolation procedure, cannot be followed. The method does not differentiate between protonated and non-protonated ions of the same degree of aggregation. It might be possible to differentiate between such ionic species by performing similar experiments in a constant electrical field.

Light Absorption

Jander has used light absorption data to supplement his diffusion coefficient data by measuring absorption of solutions adjusted to pH values corresponding to plateaus on the D.n vs. pH curves. Aggregation is accompanied in the chromate system by a shift in absorption to a higher wave length and a flattening of the peaks in the absorption curves. Similar changes in absorption are observed in these condensations. The shift in wave length is normally pronounced for the first step in the aggregation reaction. Subsequent shifts may be small. The evidence is qualitative and serves only to verify the fact that some aggregation takes place. Absorption data may be of some help in differentiating between such combinations as para and meta molybdates since the protonation changes the absorption slightly.

Conductometric Titrations

Conductometric titrations of sodium molybdates, etc. vs. added hydrogen ion yield breaks in the resulting curves corresponding either to the aggregation or protonation reactions assumed to occur on the basis of diffusion experiments. The breaks in the curve occur sharply to the ratios predicted from the diffusion experiments.

Thermometric titrations were also carried out. The curves show breaks at most of the points at which discontinuities occur in the conductance curves. Jander concludes that these processes are exothermic.

Cationic Aggregation 11,16,17,19

It has long been recognized that the formation of hydroxides of metals such as iron, chromium, aluminum, etc. cannot be represented by the simple equation $M^{+++} + 3OH^- \longrightarrow M(OH)_3$. The complexity of the solutions involved can, in many cases, be explained by assuming the presence of mono and polynuclear complexes. If such is the case, all coordinating groups within the solution (i.e., H_2O , OH^- , $M-OH$, anion) should be competing for the coordination positions and this appears to be borne out experimentally.

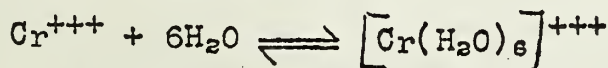
Some of the phenomena which may be explained on this basis are:

- 1) The precipitated hydroxides always contain an appreciable amount of the original anion.
- 2) These "occluded" anions are removed by washing in the order anticipated from their coordination tendencies.

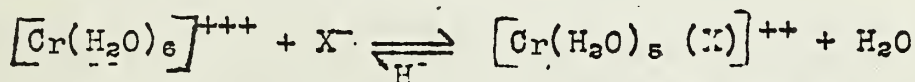
- 3) The solutions alter on standing.
- 4) The rate and nature of the changes occurring in these solutions is greatly dependent upon the anion.
- 5) Older solutions have a high buffer index.
- 6) Ionic-molecular weight measurements on basic chromium (III) solutions have yielded values of 750 or more.
- 7) The drop in pH of a Cr (III) solution upon heating and the slow rise on cooling cannot be explained by hydrolysis alone.
- 8) Up to 90% of the required amount of OH^- can be added to Cr^{+++} solutions before precipitation occurs.

While the coordination theory explains these changes it also points up the fact that this is also a case of dehydration polymerization. The following steps are considered to be important.

- 1) Hydration of the cation



- 2) Entrance of the anion into the coordination sphere. (This may occur later but is considered to take place at some time during the reaction.)



- 3) Olation--Formation of -O- bonds. Anions as well as water may be displaced on olation.
- 4) Oxolation--The formation of oxo-linkages. Oxolation is a slow process. The pH of a solution is decreased on oxolation.

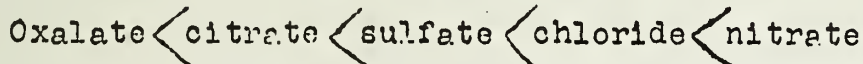
Stiasny developed a method for determining "olation" based on the fact that certain OH groups in aged solutions are less reactive toward dilute acid. Two samples of a solution are taken: 0.1N acid is added to both in excess and one is immediately back-titrated to a pH of 2.8 for Cr^{+++} . The other sample is boiled for an hour before back titration. The difference in acid used in the two cases is a measure of the extent of the "olation". From a series of experiments he determined that the following factors influence olation:

- 1) pH--All basic chromium solutions show evidence of olation which increases as the pH is increased.
- 2) The nature of the anion--sulfate solutions olate more rapidly and to a higher degree than those containing chloride. This might be due to the greater acidity of the sulfato-chromium complex. It cannot be due only

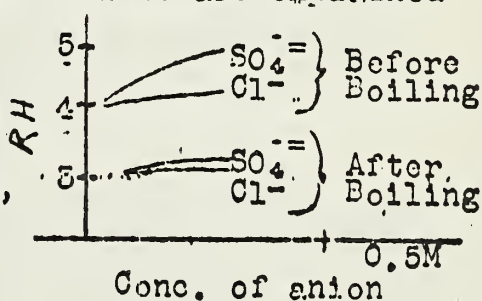
to bridging of the Cr^{+++} cations by sulfate to bring the OH groups into closer contact since carbonate, in the formation of carbonate complexes, decreases olation.

- 3) The concentration of Cr^{+++} --- Olation increases with the concentration of Cr^{+++} .
- 4) Time of aging--Olation increases with time to a maximum at 7-14 days. This time lag may be due to the slowness of oxolation and possibly to the slowness of the establishment of more stable '-ol' linkages (possibly double bridging).
- 5) Temperature--Olation increases with the temperature and on cooling decreases. As much as six weeks is required for the solution to return to its original pH.
- 6) Neutral salts--Sodium sulfate increases olation whereas sodium chloride has no effect.

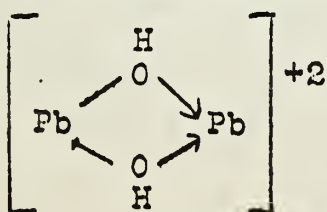
Thomas has done a considerable amount of work to show that anion effects are related to the tendency of the anion to coordinate with the metal ion. The ease of washing out the anion from the precipitated hydroxide is inversely related to its tendency to coordinate and follows the order



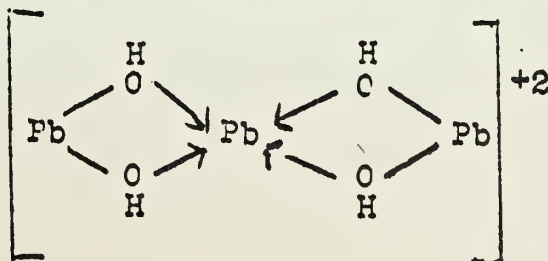
The dispersion of the solid hydroxide is also related to the tendency of the acid anion to coordinate. The fact that OH groups are tied up more strongly by olation is demonstrated by the effect of neutral salts on the pH of a hydroxide liquor before and after boiling. The relative effects of sulfate and of chloride are also demonstrated. These results are explained by assuming replacement of OH groups by anions in the coordination sphere; the number of such free OH groups is decreased during olation. These effects are general in many systems and were demonstrated experimentally for aluminum, beryllium, chromium, cobalt, thorium and zirconium salts.



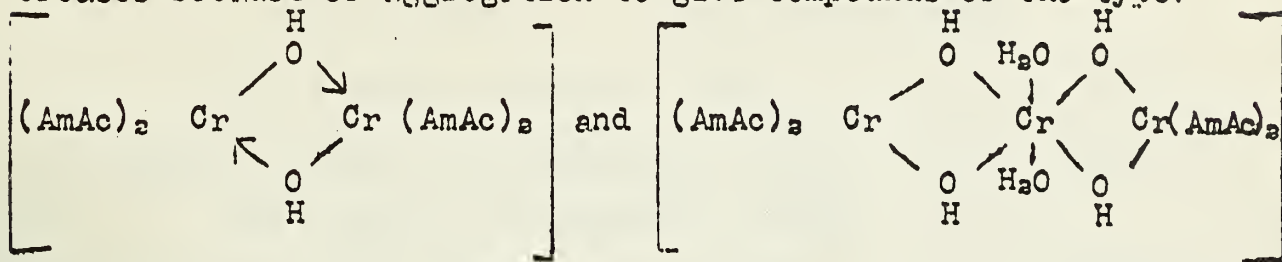
Other evidence for olation may be obtained from a study of the literature of coordination chemistry. The results of electrolysis experiments of basic lead solutions can be explained best by assuming the formation at different basicities of the ions:



and



The amino acid complexes of Cr^{+++} show that the normal complex $\text{Cr}(\text{AmAc})_3$ may be formed in the cold; on heating the solution of such a complex the N/Cr ratio in the isolated complex decreases because of aggregation to give compounds of the type:



There is some evidence that an equilibrium exists between these forms since similar mixtures can be obtained by hydrolysis of the simple coordination compounds or by treatment of the hydroxide with amino acids. Stiasny reports similar phenomena for the formate complexes of chromium. Bjerrum determined the ionic molecular weights of basic chromium solutions and obtained values up to 750 and corresponding to an average degree of aggregation of 3 to 4 units.

That there is interaction between M-OH groups in solution whether it involves coordination, or neutralization can be demonstrated by the stabilization of silica gels by the addition of hydrogen bonding agents. It is known that such interaction, i.e. hydroxyl bonding, exists in the solid hydroxides. It is interesting to note that the arrangement in solid aluminum hydroxide is that which would be predicted from the coordination theory. The structure may be represented as follows:



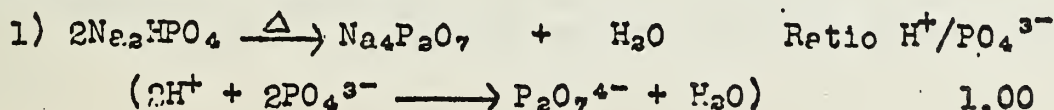
---O above the plane
 ---O below the plane of Al

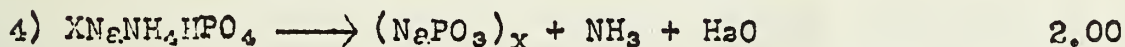
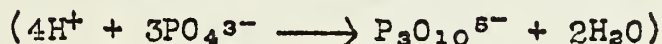
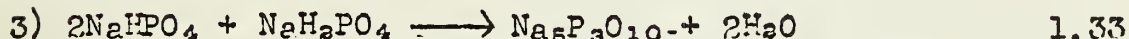
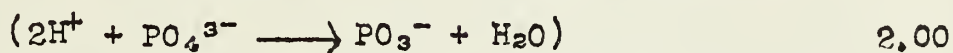
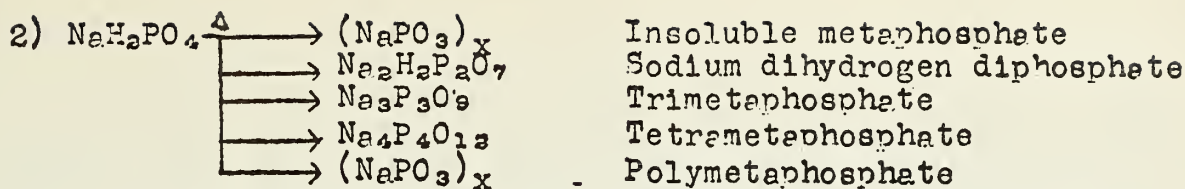
Hydroxyl bonding exists between such layers.

High Temperature Anionic Aggregation 9

The polyphosphates may be formed by thermal dehydration of acid phosphates. This may be regarded strictly as a dehydration procedure or as a condensation brought about by the presence of acidic materials in the phosphate. The acid phosphates are potential proton donors and hence acids in the Bronsted sense. These aggregation reactions may also be induced by non-protonic acids.

The following chart summarizes the reactions of the acid phosphates upon heating.





The effect of increasing acidity is obvious from equations given in parentheses.

The acid anions employed in these reactions correspond to the protonated anions postulated by Jander; the dehydration and aggregation may be considered to occur in the same fashion under the driving force of the higher temperatures.

The aggregations produced by non-protonic acids cannot be viewed in this way and is therefore of particular interest. Heating disodium monohydrogen orthophosphate alone produces sodium pyrophosphate, but in the presence of ammonium nitrate trimetaphosphate is the product. Sulfur trioxide reacts with potassium pyrophosphate according to the equation



This is analogous to the precipitation of WO_3 from aqueous solution by the addition of acid. Potassium dichromate and potassium hydrogen sulfite will convert trisodium orthophosphate to pyrophosphate at higher temperatures.

High temperature bases effect the depolymerization of the polyphosphates just as bases break up anionic aggregates in solution. The fusion of basic oxides with polymetaphosphates produces pyro or orthophosphates. Sulfides cause a similar degradation to form monothioorthophosphates. Fluoride ion is also very effective in this degradation and results in the formation of mono-fluorophosphate. The chloride ion is much less effective.

Cationic Aggregation at Elevated Temperatures: The formation of basic salts.

The formation of basic salts from hydrated salts may be considered to proceed in a manner similar to the formation of hydroxides in solution, i.e. the replacement of water in the coordination sphere by anions and the elimination of acid to leave the metal coordinated to both hydroxyl groups and anions.

Sulfur Trioxide 1,6,7,8,14,15,18

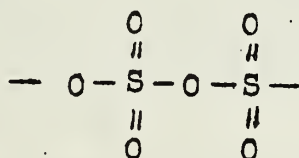
Sulfur trioxide exists in the vapor state chiefly as the monomer which is a planar molecule. Vapor density measurements indicate that only a very small degree of aggregation occurs. Raman spectra and electron diffraction patterns indicate that liquid sulfur trioxide consists of an equilibrium mixture of the monomer and a cyclic trimer with possibly some chain polymers such as occur in α sulfur trioxide. Equilibrium is established rapidly in the liquid which is therefore the same regardless of the solid form from which it is obtained.

Solid sulfur trioxide exists in three forms each of which is an equilibrium mixture of various sulfur trioxide aggregates. The establishment of these equilibria is a slow process and sulfur trioxide samples may be obtained with physical properties varying between rather wide extremes.

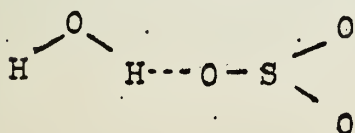
"Ice-like" or γ sulfur trioxide has an equilibrium melting point of 16.8°C and is obtained by crystallization of liquid SO_3 . Like the liquid, γ sulfur trioxide is an equilibrium mixture of the monomer and cyclic trimer. If liquid SO_3 is obtained by a condensation of the vapor, below 27°C , α and β SO_3 will also be formed.

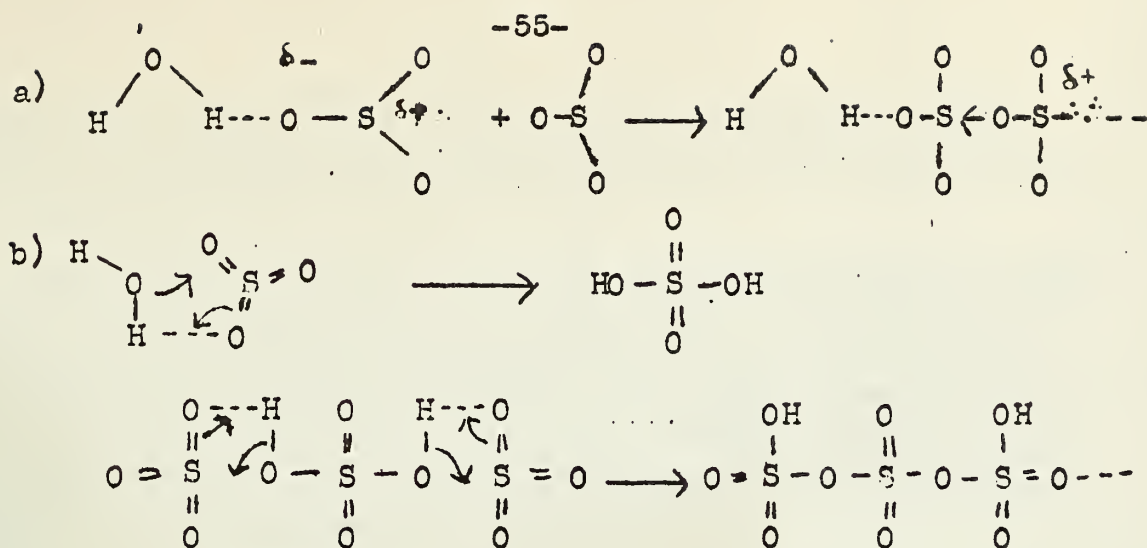
The high melting asbestos form, or α sulfur trioxide, melts at 62.3°C . It is prepared by condensing sulfur trioxide at liquid air temperatures and distilling off the more volatile fractions. It is thermodynamically the most stable form of SO_3 as is indicated by its high heat of fusion and vaporization relative to the other forms. It is an equilibrium mixture of branched chain polymers of SO_3 existing in "a layer lattice". It has been stated that SO_3 condensed at liquid air temperature possesses elastic properties characteristic of chain polymers.

The low melting asbestos form, or β sulfur trioxide, (Melting Point 32.5°C), is not a true SO_3 polymer. It is formed only in the presence of small amounts of water. As little as one molecule of water to 100,000 molecules of sulfur trioxide is sufficient to produce the β form. β sulfur trioxide is an equilibrium mixture of chain polymers in which the following unit is repeated.



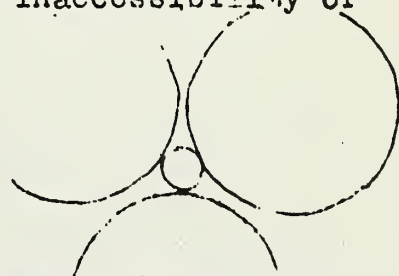
The initiation of polymerization by water may be assumed to proceed in the following way. Water could attach itself to an SO_3 molecule through a hydrogen bond. This bonding disturbs the electrical symmetry of the SO_3 molecule, creating a more positive center at the sulfur atom. From such a structure in the presence of excess sulfur trioxide, polymerization may proceed by either of two mechanisms:





It is impossible to differentiate between these mechanisms experimentally since both involve hydrogen bonding. It seems reasonable to assume that hydrogen bonding is the first step. Direct coordination of the water molecule through the oxygen atom to the sulfur is less likely considering the bulk of the oxygen atoms around the small central atom. The model shown is drawn to scale using Pauling's ionic radii and disregarding distortion. This shows quite clearly the inaccessibility of the sulfur as long as the molecule is planar and symmetrical.

It is possible that both mechanisms are applicable depending on the concentration of sulfur trioxide, (a) being dominant in high concentrations and (b) in low concentrations.



It is impossible to determine the degree of aggregation of sulfur trioxide by cryoscopic methods because of its high reactivity. Even the best results obtained using POCl_3 as a solvent indicate only five SO_3 units in the aggregates of $\alpha\text{-SO}_3$. It is generally considered that these aggregates must be much larger. Such information as is available has been gained from a study of vapor pressure, melting point and heat of solution of sulfur trioxide in sulfuric acid. More recently infra red, electron diffraction and Raman spectra studies have been made which, in general, indicate that each form of sulfur trioxide is an equilibrium mixture of "pseudo components", that this equilibrium may be disturbed in various ways with resulting changes in the physical properties of the solid, and that the establishment of equilibrium after such disturbances is very slow in the solid phase.

If either asbestos form of sulfur trioxide is volatilized slowly, the vapor pressure drops, presumably because the monomer and lower polymers are removed. The vapor pressure of the residue rises slowly along a hyperbolic curve back to a constant value. This rise in vapor pressure is facilitated by X-ray irradiation of the sample. X-ray studies indicate that this change of vapor pressure is accompanied by structural changes

throughout the solid SO_3 and is not merely a surface effect. It is safe to assume that depolymerization is taking place. The heats of solution of the SO_3 in sulfuric acid vary in such a way as to support this point of view.

The melting point of sulfur trioxide samples also varies from the equilibrium melting point to a degree dependent upon the degree of disturbance of the equilibrium. This variation of melting point has been demonstrated in the following way. A sample of sulfur trioxide melting at 65° (therefore not quite the equilibrium α form) was distilled in small quantities and the melting point of the residue recorded. The melting point rose to 95°C before all the material melted. Similar results have been obtained for β sulfur trioxide.

The stabilization of sulfur trioxide toward polymerization has been studied. Stabilized sulfur trioxide which retains the low melting point of β or γ SO_3 , even after many re-meltings, is now a commercially available product (Sulfen). Antimony pentafluoride is covered patentwise as a stabilizer in a concentration of $< 0.5\%$. The mechanism of this stabilization process is not divulged. Sulfur, selenium, tellurium and phosphorus oxychloride are also said to inhibit this polymerization but not so efficiently as SbF_5 .

Sulfur 12

The viscous, colored form of sulfur known as sulfur μ consists of long chains of sulfur atoms. Plastic sulfur, obtained by quenching this product shows elastic properties characteristic of such chains and, on being stretched, has an X-ray pattern, orientation in the same manner as rubber. Assuming that the viscosity of the S μ is proportional to the length of the chains, it can be shown that this chain length depends upon the history of the sample of sulfur employed as well as the temperature.

If virgin sulfur is employed, polymerization begins at 172° in the light and at a slightly higher temperature in the dark. The viscosity of the sulfur melt increases very markedly above this temperature indicating rapid polymerization. This can be explained by assuming that ring rupture occurs (sulfur exists in eight-membered rings at lower temperatures) to form an open chain which is probably a di free radical. The presence of this radical facilitates further ring rupture and chains result. The addition of a small amount of plastic sulfur to sulfur below 172°C produces the viscosity changes thus demonstrating the catalytic activity of some fraction of S μ in promoting polymerization. A sample of sulfur heated at 350° and cooled begins to polymerize at a lower temperature than virgin sulfur. Such a melt never becomes as viscous as a fresh melt, probably because the fragments present can also act as terminal groups besides initiating more chains thereby shortening the average chain length.

Plastic sulfur can be obtained only from slightly impure sulfur which contains oxidation products of sulfur.

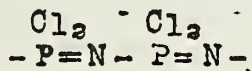
The viscosity of a sulfur melt can be controlled by addition of halogens or hydrogen sulfide which can act as terminal groups. Two percent of sulfur chloride keeps the melt mobile. Ammonia is also said to prevent the formation of plastic sulfur.

Depolymerization occurs at higher temperatures and sulfur vaporizes in the form of S_8 molecules which, upon further elevation of the temperature, break up to form S_2 . Slow cooling in the liquid state causes a reversal of the polymerization reaction to form S_8 molecules and depolymerization of the plastic sulfur occurs in the solid state.

Phosphonitrilic Chlorides 2,4,5,12

Phosphonitrilic chlorides are prepared by the ammonolysis of PCl_5 , the best results being obtained when ammonium chloride is used. A mixture of several homologous products is obtained. Two crystalline products may be isolated which have been identified as a cyclic trimer and tetramer. An oily product is also obtained from which Stokes isolated fractions to which he assigned the formulas $(PNCl_2)_x$, where x is equal to 5, 6 and 7. The residue is represented as $(PNCl_2)_{11}$.

The exact nature of these oils has never been determined, probably because of the difficulty of handling them. Stokes' analyses check very well for $(PNCl_2)_x$, but the lower $PNCl_2$ polymers must be stabilized by some sort of end groups since the polymer is composed of repeating units of the type



These oils are not so stable to heat as are the cyclic compounds and polymerize very rapidly at $200^\circ C$. to a rubbery mass. A full study of the polymerization has never been made. It is, in fact, reported largely because of its nuisance value.

The polymerization of the trimer and tetramer has been studied quite extensively because of the fact that a rubbery material can be obtained. It was thought that some commercial application could be found for this product. The results reported by various investigators are not wholly consistent, but the general pattern of polymerization appears to be established.

If the trimer or tetramer is heated in a sealed tube, oils and waxes are formed at about 250° if heating is continued for about five hours. Polymerization is rapid at 300 to $350^\circ C$. and the inorganic rubber is produced. It is assumed that the first step of this polymerization is ring rupture which is followed by chaining of the fragments so formed. It is reported that ultra-violet light and water facilitate this ring rupture. The temperature, time of heating and pressure affect the nature of the product.

This polymerization is apparently a reversible reaction. At least, if the condensation is carried out in the vapor phase at 600° an equilibrium mixture of oils, waxes, trimer and tetramer is obtained. The addition of trimer to this system causes the anticipated shift in concentration of these fractions. The fact that the inorganic rubber always contains some trimer and crystallizes on long standing supports this point of view. This depolymerization is not a clearly defined process in the case of PNCl_2 polymers; the partially fluorinated polymer depolymerizes readily to the tetramer.

Above 350°C. the inorganic rubber depolymerizes to yield the lower homologues, principally the trimer. If a sample of the rubber is heated in a vacuum, no residue is left. Slow heating of this polymer at atmospheric pressure to red heat produces a brittle mass which does not change on further heating. The nature of this material has not been determined, nor is it stated whether it can be made to produce PNCl_2 on heating in a vacuum.

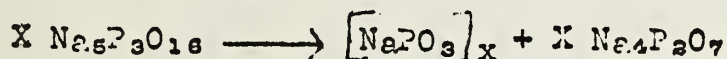
X-ray studies of inorganic rubber show it to have a random arrangement when not under stress, but it consists of oriented fibers when stretched. It is estimated that each fiber contains more than 200 PNCl_2 units. This polymer has elastic properties similar to those of rubber as can be demonstrated by the similarity of the torsion-temperature curves for these two materials.

The chlorine atoms in PNCl_2 are active and may be replaced by OH, NHR, OR or OAr either prior to or during polymerization. Recent experiments have been carried out using negatively substituted phenols and acetanilides to produce substituted P=N polymers. In most cases a brittle, thermoplastic resin is obtained. These resins may be colored, depending on the nature of the substituted group.

The lowest stable form of PNCl_2 is the trimer, yet a monomeric form is apparently stabilized by coordination with tertiary amines to form compounds of the type $\text{PNCl}_2 \cdot 2\text{NR}_3$. These compounds are extremely reactive as might be expected. The formation of such compounds may lend credence to the statement that dioxane, another coordinating agent, facilitates the depolymerization of the inorganic rubber.

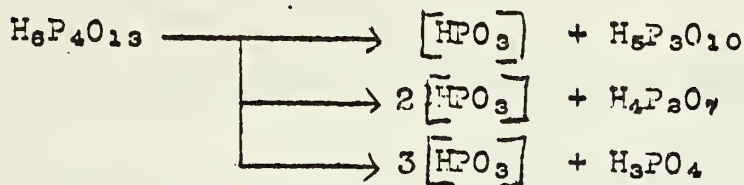
Disproportionation Polymerization

It has long been known that sodium triphosphate undergoes disproportionation when heated to above 620° to give

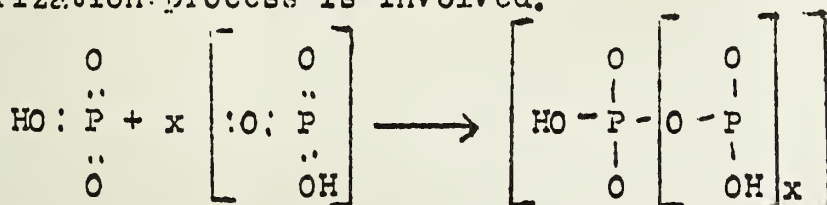


On heating crystalline pyrophosphoric acid mixtures of ortho, poly and meta phosphoric acid are obtained. Only after long standing does solid $\text{H}_4\text{P}_2\text{O}_7$ reform as a crystalline phase. The tendency to disproportionate increases with rising temperature.

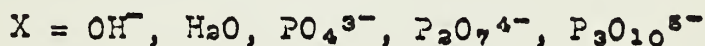
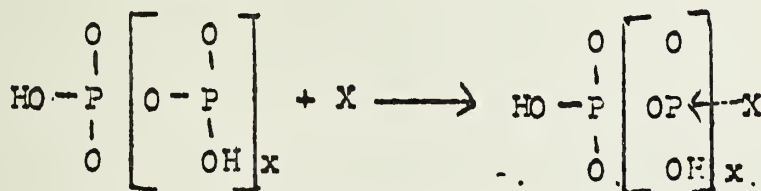
Compounds which might be expected to give tetraphosphoric acid or a tetraphosphate appear to undergo molecular disproportionation into smaller as well as larger molecular species in accordance with several possibilities:



The monomeric HPO_3 fragments appear as polymetaphosphoric acid of high ionic molecular weight. Such a polymerization is similar to a free radical type process except that free radicals cannot logically be postulated. Stabilization by a coordination type polymerization process is involved.



Molecules such as water or ions such as the stable linear phosphate or hydroxyl ions act to terminate the polymerization process (chain breakers).



This concept of a strictly inorganic polymerization process is offered as an explanation of the observed phenomena.

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December 19, 1950

GLASS FORMATION IN NON-SILICATE SYSTEMS

The glassy state can be easily recognized by typical properties such as hardness, brittleness, optical homogeneity, isotropy, conchoidal fracture and by lack of sharp x-ray diffraction patterns. However it is difficult to define a glass uniquely or to bracket a substance as glass forming. Attempts to define a glass by its energy content, or by a continuous change in its properties with temperature as compared with abrupt changes shown by crystalline materials are not successful.

Most glasses are thermodynamically unstable, their energy content being higher than that of the crystalline phases of the same chemical composition. As a result glasses are usually more soluble, have a higher vapor pressure and are chemically more reactive than their crystalline modifications. However this is not always true. Glassy P_2O_5 has a higher density than one of its crystalline modifications, is less soluble (in $CHCl_3$) less reactive, and has a lower vapor pressure than the crystal.

A glass softens gradually and does not have a sharp melting point. However silver iodide also softens gradually and can be easily deformed below its melting point and albite, a crystallized sodium aluminosilicate, can be kept at 50° above its melting point for many days and does not lose its crystal-optical characteristics nor its crystalline outline. The "abrupt" change versus the continuous change cannot therefore be used in defining glasses.

It is likewise impossible to describe glasses from the viewpoint of chemical composition. Elements (Se), halides (BeF_2), oxides (SiO_2 , P_2O_5 , B_2O_3), sulfides (SnS_2 , As_2S_3 , Sb_2S_3), salts of oxy acids ($NaPO_3$), coordination complexes (Na_2BeF_4), and numerous organic compounds (glycerol, sugar) may be obtained in the vitreous condition.

In order to define a substance as "glass forming" the time element must be taken into consideration. Many substances which can be obtained in the vitreous state in small quantities in the laboratory crystallize when subjected to the temperature-time schedule of commercial glasses. Sodium metasilicate, Na_2SiO_3 , for example, forms a glass when a few grams are fused and allowed to cool. In greater quantity, crystallization is unavoidable. Thus, the quantity of substance which in turn affects the cooling rate is a factor in glass formation. The number of glass forming compounds become very large indeed if microscopic dimensions and high cooling rates are employed. Tammann and Elbrächter (1) made microscopic glass beads from a number of substances which in gram quantities cannot be obtained in the vitreous state. Among them were alkali nitrates and silver halides.

THEORY OF GLASS FORMATION BASED ON CRYSTAL CHEMICAL CONDITIONS.

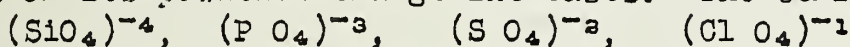
With the development of modern crystal chemistry observations on the known glass forming materials have led Goldschmidt (2)

and Zachariassen (3) to postulate a series of rules. Goldschmidt pointed out that glass forming oxides have a radius ratio, $R_{\text{cation}} : R_{\text{O}^{2-}}$ of approximately 0.3. This condition is conducive to tetrahedral arrangements and indeed most glasses consist of XO_4 groups as the elementary building units. On this basis Zachariassen proposed the following rules governing glass formation in oxides.

- 1) A low coordination number of the cation is essential (3 for boron and 4 for most glass forming oxides)
- 2) The XO_4^{n-} tetrahedra share only corners, not edges or faces.
- 3) The O^{2-} ion can not have a coordination number higher than two.

The sharing of corners produces a random and slightly distorted network which should have a slightly higher energy content than the crystalline arrangement.

It has furthermore been postulated that for glasses built up from XO_4 units, the cation to anion ratio must be at least 1:2. Al_2O_3 cannot form a glass because the C:A ratio is only 1.5. The Al^{3+} cation requires fourfold coordination with oxygen. Boric oxide, B_2O_3 has the same C:A ratio but can form a glass because the small size of the B^{3+} ion allows threefold coordination whereas in crystals the XO_4 unit represents a self repeating group with constant X-O distances, this is not true for glasses. The randomness of the glass structure causes the building units to be slightly distorted so that the internuclear distances show a certain spread. For this reason only those polyhedra which are easily distorted are suitable to form a glass. The energy requirements for the distortion of an XO_4 tetrahedron increase with the force field of the central cation. The force field of the central cation, in turn, increases as its size decreases or its positive charge increases. The series



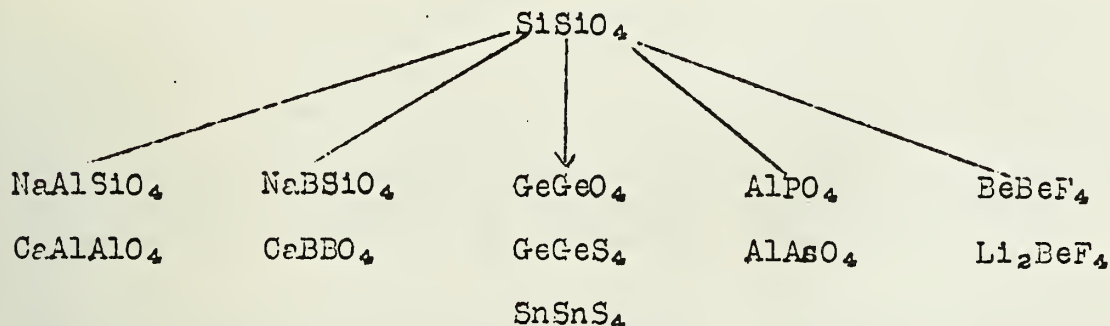
represents XO_4 tetrahedra where the central cation has the electron configuration of the neon atom. The Cl^{+7} is the smallest and most highly charged cation, and, consequently, it exerts the strongest positive force field. Perchlorates are not known in the vitreous state.

The sulfate group is not easily distorted because of the strong field of the S^{+6} ion. However, Weyl and Forland (4) succeeded in causing distortion and consequent glass formation by producing a strongly asymmetrical force field around SO_4^{2-} by combining the strong positive field of the small proton (H^+) and the weak positive field of the large K^+ . The symmetry of the sulfate group can also be decreased by replacing one of the four O^{2-} ions by another ion such as S^{2-} as shown by the glass forming thiosulfate group $(\text{S}^{+6}\text{S}^{2-}\text{SO}_3^{2-})^{2-}$. Distortion by secondary cations with widely different force fields has been used by Shaliks (5) to produce a vitreous carbonate, $\text{K}_2\text{Mg}(\text{CO}_3)_2$, and Bergmann (6) to produce a vitreous nitrate, $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$.

SURVEY OF INORGANIC GLASSES (7)

A brief survey of the inorganic glasses can be used to give further examples of the preceeding postulates. The scheme in Table I may be used as a guide. Silica is represented by the formula SiSiO_4 to indicate replacement of one or both Si^{+4} by other cations in the formation of other glasses.

Table I



By replacing one Si^{+4} ion by an Al^{+3} ion and adding a monovalent cation for maintaining electroneutrality an aluminosilicate glass is obtained. Bussem and Eitel (8) discovered that fusions of CaO with alumina form glasses on cooling. In the atomic structure of these glasses AlO_4 tetrahedra take the place of the SiO_4 tetrahedra. Pure aluminate glasses are readily attacked by acids and are therefore not used commercially.

If the couple Na^+B^{+3} is substituted for part of the Si^{+4} the important borosilicate glasses are formed. The reaction is easily possible at the high temperatures of melted glass. Ionic rearrangement occurs at lower temperature regions allowing alkali borate crystal formation in the glassy silica matrix. This is the process used for the Vycor glasses. Complete substitution of boron for silicon leads to a group of borate glasses which when mixed with the rarer elements (La, Th, Ta) form important optical glasses with high refractive indices and low dispersion power. (9)

Although phosphate glasses are well known and have enjoyed early use due to their high index of refraction, high transmittance of ultra-violet light and resistivity toward HF, they have now been replaced by the more stable aluminophosphate glasses. Grimm and Huppert (10) were able to prepare AlPO_4 glass by use of unequal force fields of Al^{+3} and P^{+5} . The optical properties of quartz and AlPO_4 are nearly identical and the two compounds have the same hardness. The dimensions of their unit cell are identical in two directions, but in the direction of the c axis the length of the unit cell for AlPO_4 is twice that of quartz so that each cell can accommodate an Al^{+3} and P^{+5} ion. (11)

Silicon can easily be replaced by the larger Ge^{+4} ion to form GeO_4 glasses which due to their close similarity to SiO_2 and greater cost have no practical applications. However the Ge^{+4} ion is sufficiently large to form a yellow GeS_2 glass described by Pugh (12). It is to be noted that Si^{+4} is too small to form a sulfide glass in the same manner that C^{+4} is too

small to form an oxide glass. According to Tammann (13), the sulfides of tin, arsenic, and antimony form glasses. Because of their absorption in the visible region these glasses have not been used in optical glasses and therefore not studied systematically. Present interest is demanding a more thorough investigation of the complex sulfide glasses. Weyl proposes that similar asymmetrical force fields could be used to stabilize the vitreous sulfides of Ge^{+4} , Ti^{+4} , Sn^{+4} , Sb^{+3} , and Ss^{+3} and further modification could be attained by replacing the sulfide ion by Se^{-2} and Te^{-2} .

The theory of "model structures", first introduced by Goldschmidt to explain isomorphism of such crystalline substances as CaF_2 and ThO_2 has been used successfully to prepare new glasses. "Model structures" are compounds having the same crystal structure but different valence sums. The structure with the higher valence sum is the stronger model. This can be shown by the higher melting point, greater hardness, and insolubility of ThO_2 over its weaker model, CaF_2 .

BeF_2 , the weaker model structure of SiO_2 , and $\text{K Li Be}_3 \text{F}_8$, the weaker model structure of feldspar, $\text{K Al Si}_3 \text{O}_8$, were found to have the same crystal structure. The fluoro-beryllate glasses are highly desirable due to their low refractive index (lower than those of H_2O) and dispersion, low softening point ($160-300^\circ$), and high ultraviolet transmission. Of further interest is the fact that fluoroberyllates are miscible with the phosphates and sulfates and can therefore be expected to form glasses with these established glass formers.

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CHEMISTRY INVOLVED IN THE FORMATION OF THE EARTH

Fred L. Pundsack

January 9, 1950

One of the first truly scientific attempts to explain our solar system was the nebular hypothesis proposed in 1796 by the French astronomer Laplace. This was supplanted in the nineteenth century by the famous Jeans-Jeffreys hypothesis, which in turn was followed in 1905 by the Chamberlain planetesimal hypothesis (4).

A common feature of all of the preceeding hypotheses is the fact that the original Earth is depicted as condensing from a body of hot gases. In some of these hypotheses the term "hot" is not defined precisely, but in all cases it certainly is intended to mean a temperature in excess of at least 5000-6000°C. In contrast to these views is the hypothesis, put forth recently by Latimer, which assumes that the Earth was formed by condensation of a "cold" cosmic cloud (6). Latimer contends that the presence of water and the absence of quantities of the noble gases, the constant isotopic composition of matter in the Earth and in meteorites, and the presence of both oxidized and metallic iron are more readily explained by his cold cosmic cloud condensation view than by any of the preceeding hot gas condensation hypotheses.

Since direct experimental observation of the interior of the Earth is not possible, all concepts of the internal structure of the Earth must possess a somewhat speculative character. However, these speculations have a fairly sound basis in certain experimental observations such as seismic recordings, velocity of earthquake waves, calculations of the average density of the Earth, and analysis of meteorites. Meteorites are believed generally to be fragments of a member of our solar system. In any event analogy is drawn between the composition and structure of meteorites and the internal structure of the Earth. Meteorites are classified into three main groups according to the predominance of the metallic or silicate phase: 1. irons or siderites; 2. stony-irons or siderolites; 3. stones or aerolites. Evidence seems to indicate that these three general groups originated from different depths within the source planet. Thus the starting point for most hypotheses regarding the internal structure of the Earth is to view the Earth as composed of a number of concentric shells of roughly similar phase. Seismic recordings, the velocity of earthquake waves, etc. seem to support this picture.

One of the first attempts to correlate the composition of meteorites with the internal structure of the Earth was that made by Washington in 1925 (8). He depicted the earth as made up of about six concentric shells beginning with an inner core of metallic iron and nickel and progressing outward thru various metal + metal-silicate phases to the outermost granitic shell.

A better known attempt to correlate the internal structure of the Earth with the composition of meteorites is the hypothesis of Goldschmidt (7). Goldschmidt attempted to draw an analogy between the Earth and an ore-smelting furnace. He depicted an inner core containing 90% iron, 8% nickel, and 2% other metals. Around this core is an intermediate sulfide layer composed largely of sulfides and oxides of iron. Beyond this is an outermost shell, called the lithosphere, composed of silicates. However, Goldschmidt did not believe that any of these phases were completely separated from the other and therefore no absolutely distinct shells were formed.

A third structural hypothesis which has as yet received little attention is that of Kuhn and Rittmann (5) which assumes that the center part of the earth is composed of original solar material containing at least 30% hydrogen.

Neither the hypothesis of Washington or of Goldschmidt agrees with the present information about the physical properties of the Earth's interior. The variation of the velocity of earthquake waves with depth indicates a number of discontinuities at definite depths representing sudden changes in physical properties. Whether or not these discontinuities are caused by changes in the state of aggregation or by actual changes in chemical composition has not yet been established.

Two main "first-order" discontinuities have been characterized in the Earth's interior; the Mohorovicic discontinuity at a depth of 30-50 km and the Wiechert-Gutenberg discontinuity at a depth of 2900 km. On the basis of these discontinuities the Earth is divided into three main spheres:

1. Core - extends from center of the Earth to Wiechert-Gutenberg discontinuity.
2. Mantle - occurs between the two first order discontinuities.
3. Crust - from the Mohorovicic discontinuity to the surface.

So called second-order discontinuities have been recorded within these three main shells.

The center core of the Earth is believed to consist of nickel-iron corresponding to so-called pure iron meteorites. Second-order discontinuities within this core indicate a subdivision into two parts due to occluded gas in the outer core. Most opinion agrees, in principle at least, to a silicate mantle. At greater depths the silicate material exists with interstitial iron and nickel, the interstitial metal increasing with increasing depth. The main silicate phase also becomes poorer in the lighter elements with increasing depth. The Earth's crust consists of two main areas: the Pacific basin existing as one area while the remainder of the Earth's surface constitutes the other area.

In his cold cosmic cloud hypothesis, Latimer believes that the composition of the Earth is essentially that of the

solid particles which he assumes are present in such a cloud. Latimer is enabled to draw conclusions as to the composition of the cloud by using the table of relative cosmic abundances published by Brown (2).

COSMIC RELATIVE ABUNDANCES

Element	Abundance (atoms/10,000 atoms Si)	Element	Abundance (atoms/10,000 atoms Si)
H	3.5×10^8	Na	462
He	3.5×10^7	Cl	190
O	210,000	P	130
N	160,000	Co	99
Ne	$10^4 - 10^5$	Cr	95
C	80,000	F	90
Fe	18,300	Mn	77
Si	10,000	K	69
Mg	8,870	Ti	26
S	3,500	Cu	4.6
Ni	1,340	V	2.5
A	130-2,000	Zn	1.6
Al	832	Ga	0.65
Ca	670	Sc	0.18

Latimer assumes that the preceeding elements are present in the cosmic cloud at a temperature of not more than a few hundred degrees Kelvin. Through application of chemical thermodynamics he concludes that the cloud will contain the following:

Gases

Solids

H ₂	Metals as Fe and all less electropositive elements
H ₂ O	Oxides or their cpds. of Fe, and all elements more electropositive than Fe (e.g. Fe ₂ SiO ₄ , MgSiO ₃ , Ca ₂ (AlO ₃) ₂ · nH ₂ O)
CH ₄	Nitrides - Fe ₂ N ₃ , etc.
NH ₃	Carbides - Fe ₃ C, etc.
He, Ne, ... etc.	Halides - CaF ₂ , NaCl, NH ₄ Cl, etc.
	Sulfides - FeS, PbS, etc.

The gaseous materials present will have several hundred times the mass of the solid particles. Due to the large excess of H₂ and H₂O, stabilities are determined by oxidation-reduction potentials relative to these substances.

Latimer places a great deal of emphasis upon the problem of iron and ferrous oxide probably because it allows him to relate his theory to experimentally observed conditions in meteorites. He concludes that FeO is actually combined with SiO₂ to form FeSiO₃ which would be stable under

the conditions postulated. Thus the amount of oxidized iron depends upon the amount of SiO_2 available for formation of iron silicates. The amount of SiO_2 available depends, in turn, upon the amount of magnesium present. Thus, in the final analysis, the amount of oxidized iron depends upon the amount of magnesium present and it is possible to calculate a theoretical ratio of magnesium to oxidized iron which is in fair agreement with similar experimental ratios determined for meteorites.

The "earth cloud" probably originated from the breakup of a larger cloud which was the origin of the other planets. If this hypothesis is true the smaller planets should have condensed to bodies without atmospheres because their mass was insufficient to hold most of the gases present. On the other hand, the major planets had sufficient mass to hold the gases in the cloud and thus their composition should approximate the total composition of the initial cloud. It is actually known that the structures and atmospheres of the minor or Earth-like planets (Mercury, Venus, Earth, Moon, Mars, and Pluto) differ quite markedly from those of the major planets (Jupiter, Saturn, Uranus, and Neptune). The former have average densities of the same order and with the exception of the Moon and perhaps Mercury are assumed to have iron cores and silicate mantles in much the same fashion as the Earth. The Moon and Mercury are believed to be composed entirely of silicates. On the whole the Earth-like planets have relatively thin atmospheres differing in composition from planet to planet. With the exception of Earth, no planet possesses an atmosphere containing oxygen in amounts detectable by spectrographic means. For example spectrographic evidence tends to indicate that above the cloud layer of Venus the atmosphere consists mostly of CO_2 . There is no evidence for oxygen or water vapor. Mars has an atmosphere the bulk of which probably consists of nitrogen.

The average densities of the major planets are much lower than the average densities of the Earth-like planets. They are believed to have small dense cores probably of iron with a thin silicate layer, the whole structure constituting no more than 20% of the volume of the planet. The other 80% has been depicted as a vast layer of ice several thousand kilometers thick overlaid with an envelope of highly compressed gases (mainly H_2 , but also He, Ne, N_2 , and CO_2) (12), or assuming that the amount of oxygen originally present was too small to permit the formation of a thick ice layer, the outer shell is hypothesized as consisting of permanent gases in a highly compressed or even solidified state (13). The atmospheres of the major planets are very thick and due to the degree of compression their viscosity approaches that of common liquids. The atmospheres of Jupiter and Saturn contain both methane and ammonia, while only methane has been detected so far on Uranus and Neptune.

To return to the condensation of the "earth cloud" itself - Latimer believes that during its condensation under gravitational forces to form the Earth, two important processes occur: (1) loss of gaseous material; (2) concentration of iron particles toward the center of the mass.

The gases escape because the gravitational forces at the surface of the condensing "earth-cloud" are insufficient to hold them. Latimer treats the condensing solid particles during the major portion of condensation as particles "falling" through an appreciable concentration of gases, and thus it is possible to use Stokes' Law in determining the velocity of fall. Stokes' Law:

$$V = \frac{2a^2 (d-dm) G}{9 \eta}$$

a = radius of particle
d = density
dm = density of medium

G = acceleration of gravity
 η = viscosity coefficient

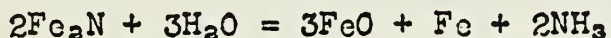
Under a given set of conditions the velocity of fall will depend largely upon the size and density of the particles, thus it seems logical to assume that the iron concentrated at the core with heavy silicates around it and the lighter basalt nearer the surface.

Since he has hypothesized a cold condensation, Latimer accounts for the present internal temperature of the Earth as the result of the heat evolved from certain radioactive decay processes. Particular emphasis is placed upon the decay of K^{40} , and a set of calculations is made which indicates that the radioactive decay of K^{40} alone since the assumed beginning of the Earth has been sufficient to account for an increase in temperature of the mantle of more than 1000°C .

After the initial formation of the Earth, the increase in internal temperatures brought about some significant changes. The granite of which the continents are composed was formed by decomposition of some of the basalt layer. Surface water was formed by rising steam which had been liberated by the breaking down of hydrated silicates and aluminates. Many carbides were oxidized by ferrous oxide:



The free iron formed by this reaction was reoxidized to ferrous oxide by part of the rising steam. Ammonia was formed by the steam hydrolysis of nitrides:



In the hot regions the NH_3 would decompose into N_2 and H_2 .

At his stage the atmosphere consisted of water vapor, CO_2 , N_2 , H_2 (slowly lost from the gravitational field) and perhaps some NH_3 . Our present supply of oxygen resulted from photochemical processes. Any NH_3 originally present has since been oxidized by oxygen. Large amounts of CO_2 were absorbed by such basic oxides as CaO and MgO which had been liberated by the hydrolysis of the complex silicates.

One of the major difficulties encountered by Latimer's hypothesis is the fact that during the condensation process the gravitational energy is sufficient to heat the whole mass to thousands of $^\circ\text{K}$ unless it is dissipated in some manner. Latimer sets out to prove mathematically that because of the fairly high viscosity coefficients and low terminal velocities of the cloud particles the rate of fall of particles of radii less than 10^{-3} cm. is so low that the particles do not acquire a high temperature in their slow fall to the Earth's surface. The proof is not completely satisfactory.

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ELECTRODEPOSITION OF ALLOYS

Fred McCollough

January 16, 1951

Two or more metals may be deposited from an electroplating bath only under special conditions. If two soluble metal salts of different metals are taken at random, it is unlikely that the metal ions will codeposit when an electric current is applied across the electrolyte. Experimentally, it is true that an alloy deposit could eventually be obtained by trying enough combinations of metal salts; but the deposit would be of commercial value only if it were sound and if the conditions were practicable from the standpoint of control and reproduction.

The most successful alloy plating baths have been those that are similar to single metal baths, with the addition of a second soluble metal. The same principles that apply to single metal deposition, apply to alloy deposition. The same few variables control both. In order to codeposit two or more metals, the several variables must be combined in a way that causes the several metals to have the same deposition potential. For example, by controlling the concentrations of the ions, it is possible to codeposit Cu-Zn alloys. Even though the deposition potentials of Cu and Zn differ widely in acid solution (+0.3v. and -0.6v. respectively), in a basic cyanide solution their d.p. are essentially the same (-1.0v).

In an alloy plating bath, the single electrode potentials, E^s , of the metals, as given by equation (I) are generally fairly close together.

$$\text{Eq. I} \quad E^s = E^\circ - \frac{RT}{nF} \ln a^{v+}$$

This is oversimplified since equation (I) refers to a static condition of reversible equilibrium. Since deposition usually occurs in an irreversible process, equation (I) can't indicate the deposition potential, which is a dynamic value associated with the discharge of cations at a definite rate. The deposition potential, E^d , as given by equation (II) includes a term P.

$$\text{Eq. II} \quad E^d = E^\circ - \frac{RT}{nF} \ln a^{v+} + P \quad (\text{where } P = \text{or} > E^d - E^s)$$

a^{v+} = activity of depositing cation

P = rate factor expressed as the extra potential required to keep deposition going at given speed.

Equation (II) and single deposition measurements are of only indirect use in alloy plating because of the influence of metal ions on each other's activities when more than one ion is present in the cathode film.

Parks and LeBaron⁴ have empirically developed an equation that is interesting in the study of alloy deposition. The limiting concentration of the second metal in the bath at which pure second metal will deposit is shown as a function

of the valences of the two metals, the difference in single deposition potential, the equivalent weights and the cathode current density, where mono- and bivalent metals are depositing in acid baths.

$$\frac{C_1}{C_2} = \frac{aZ_1^2 - bZ_2^2}{Z_2^2 + cZ_1^2} \cdot \left(\sqrt{\frac{I}{N}} \right) \cdot \frac{E_1}{E_h} \cdot \log \text{ c.d.}$$

C_1 = conc. of cation of lower cathode potential

C_2 = conc. of cation of higher cathode potential at the limit of codeposition

Z_1 = valence of ions of lower cathode potential

Z_2 = valence of ions of higher cathode potential

N = difference in cathode potentials of pure metals at a given c.d.

E_1 = Eq. wt. of metal of lower cathode potential

E_h = Eq. wt. of metal of higher cathode potential

c.d. = current density (m.amp/cm²)

a, b, c = empirical constants

When problems of physical conditions of the plate arise, the alloy platers can turn to tricks such as use of addition agents, changing pH, changing degree of agitation, temperature etc. These are some of the reasons why each alloy plating problem is solved only by experiment.

The anode process in alloy deposition is equally as important as the cathode process. The anodes can be either:

- 1) soluble alloys
- 2) soluble, separate anodes of each metal
- 3) insoluble, with metal make-up by addition of suitable compounds of the metal
- 4) a combination of 1, 2, and/or 3

Alloy anodes provide the simplest control. However, problems do arise because of phasial, physical or chemical difficulties. A single phase, solid solution type of alloy anode is normally expected to be most satisfactory. Alloy anodes have been used in depositing several different compositions of Cd-Ag alloys; and they are used in brass deposition.⁵

Whenever there is a wide difference in the relative mobility of two metals in an alloy plating bath, separate soluble anodes of the two metals should be considered. The metal dissolution ratio and rate are controlled by carefully maintaining

- 1) the current density to each of the two anodes.
- 2) the potential drop between the two different anodes.

- 3) the potential drop between the cathode and anodes
- 4) the proper placement of the anodes in the tank so that anodes on one bus bar do not receive series current flow from anodes on the other bar.

This method of single metal anodes is being used successfully, for example in Cu-Sn alloy plating⁶; but requires more exacting control than that of alloy anodes.

The third type of anode system, that of insoluble anodes, is used successfully in a few cases, but isn't applicable to heavy, continuous production because of build up of anion concentrations. A modification of this type of system uses an anode of one metal only, with the second metal being added as a soluble salt. This process is widely used when the second metal is relatively small in amount.⁷

In general, the constituents of alloy plating baths can be divided according to function:

- 1) the primary salts, which provide the primary ions
- 2) secondary salts, which influence the ionization of the primary ion source
- 3) addition agents controlling the form of the plate
- 4) buffer compounds
- 5) conductivity salts
- 6) salts promoting anode solubility

Primary salts have already been discussed. Secondary salts are those of non-depositing metals with or without a common anion. These salts are necessary to improve conductivity and/or anode solubility. The main function of an addition agent is to produce sound metallic deposits of desired physical properties. Addition salts such as alkali chlorides, Rochelle salts, and fluorides have the important purpose of promoting anode solubility of the metals in the desired ratio.^{8,9}

The influence of variables in alloy deposition can be considered effectively in terms of the relative nobility of the codepositing metals. By noble metal, we mean the metal that has the greater tendency to plate in competition with a second metal. The ratio in which two metals are codeposited depends on the combination of several variables. An increase in current density tends to increase the proportion of the less noble metal in the alloy plate. An increase in agitation usually increases the amount of more noble metal in the alloy plate. An increase in temperature usually tends to increase the proportion of more noble metal in the alloy plate.

Alloy deposition in practice and research has shown some definite advantages. In general, one may expect alloy plates to be denser and harder than plates of the single metals involved. In certain composition ranges, alloy deposits have been found brighter than either metal alone, more corrosion resistant, tougher and more adherent to the basis metal than is one or both of the individual metals alone.^{10,11}

Electrodeposited alloys are produced cold, hence need not be subjected to undesirable heating. Cu-Zn alloy of exact composition has been deposited for many years as a bonding layer for rubber coating of steel. Another application provides a Ag-Cu alloy for an undercoat for enamel. Solder refining and manufacture by electrodeposition have been done for many years. More recently, alloy powders have been prepared electrolytically.^{12,13}

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PRODUCING A SYNTHETIC DIAMOND

Merle L. Winters

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The perfection of crystal structure, hardness and various optical properties are only a few of the many interesting properties displayed by the diamond. Because it is such an interesting material and, also, because of its "rarity" and expensiveness in comparison to demand, it has long been a challenge to scientists to produce the diamond synthetically.

Many investigators worked on this problem with varying reports of success before very much was known about crystal structure and the thermodynamics involved in the transformation of amorphous or graphitic carbon to the diamond allotrope. Now, however, sufficient data are available to calculate the free energy change (ΔF) of the transition at various temperatures and pressures. From these calculations it is possible to get an idea of the pressures and temperatures necessary for the conversion to take place.

Table I summarizes the data obtained by F. D. Rossini and R. S. Jessup⁵ in regard to the change in free energy of the transition. A decrease in free energy, of course, must result for diamonds to be formed.

Table I

Reaction	ΔH_2 as is cal/mole	ΔF_2 as is cal/mole
C, graphite + O ₂ , gas = CO ₂ , gas	-94,030 ± 11	-94,239 ± 14
C, diamond + O ₂ , gas = CO ₂ , gas	-94,484 ± 28	-94,925 ± 28
C, graphite = C, diamond	454 ± 30	686 ± 31

These values are based on the determination of the heats of combustion and entropies of very pure graphite and diamond.

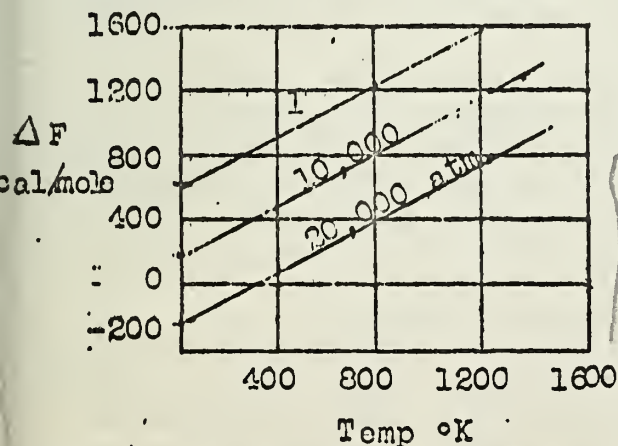


Fig. 1. Free energy change of the transition graphite to diamond as a function of absolute temperature.

Figure 1⁵ is a plot of the free energy change of the transition, graphite to diamond as a function of temperature at different pressure. Rossini and Jessup conclude that there is no temperature at which diamond is stable with respect to graphite below a pressure of about 13,000 atmospheres. At 300°K a pressure in the vicinity of 16,000 atm. is calculated to be necessary to produce equilibrium and at 470°K 20,000 atm. of pressure is required.

Some investigators mention the velocity of transition as an important theoretical consideration but this writer has been able to find nothing more than verbal observations as to its effect. A common element of the procedures tried seems to be the sudden subjection to the great pressure needed.

The actual mechanism of change that takes place in the valence bonds when transformation of graphite to diamond is made is also obscure. In diamond, each carbon atom is surrounded in the tetrahedral configuration by four other equi-distant carbon atoms, an extension of which produces an infinite three-dimensional structure. In graphite, the carbon atoms form hexagonal rings which lie in planes so that a carbon atom in a ring is surrounded by three other equidistant carbon atoms in the same plane. The fourth bond that the atom is able to share is directed to a carbon atom in another plane and is at right angles to the other, much stronger coplanar bonds. The C-C bond distance in diamond has been determined as being 1.54 A.U. In graphite the coplanar bonds are 1.42 A.U. and the extraplanar bond is 3.40 A.U.² A close study of models of the two structures will give one more of a feeling of similarity between the two than only a casual glance produces. Slight mental projection of certain atoms into a planar six membered ring structure from the diamond structure gives one the image of the graphite structure. In other words, it is possible to identify a distorted six-carbon ring in the diamond lattice.

The first investigators of this problem had only a vague knowledge of the natural formation of diamonds to guide them in their work. The presence of varying amounts of iron as an impurity in many natural diamonds led some to try recrystallization from molten iron. Others duplicated the mineral formation (known as blue-ground) from which most diamonds are mined.

The first experiments resulting in the reportedly successful synthesis of diamonds were carried out by J. B. Hannay in 1880.³ His method involved the heating of a mixture of 90% paraffin spirit and rectified bone oil with lithium. The function of the lithium is probably to combine with hydrogen and nitrogen atoms. The mixture was sealed in a thickwalled iron tube and heated at dull red heat for about fourteen hours followed by slow cooling. This method was repeated about eighty times and, of the experiments that didn't go askew before recovery from the cooled iron, Hannay claimed that three resulted in successful synthesis.

Henri Moissan reported in 1893 that he had been successful in producing the diamond by heating a carbon crucible containing pure iron and charcoal in an electric arc furnace. When the material was at white heat he quenched it in a bath of molten lead.⁴ The small crystals found among the residual carbon were proved by all tests known at that time to be diamonds.

J. W. Hershey,⁵ after repeated unsuccessful attempts, reported his first successes in 1929 and continued to report on the problem until his death just a few years ago. He varied the conditions of his experiments considerably; using vegetable compounds, sugar carbon, coal, wood charcoal and coke as sources

of carbon and copper, silver, lead, nickel-steel, manganese steel meteorite iron, tungsten and "blue-ground" as solvents for the carbon. Best results were obtained with the iron and steels as solvents. The mixtures were heated in synthetic graphite crucibles for over an hour at 3000 to 4000°C. and were usually quenched in an ice-cold brine solution. It was also implied that some success was achieved when the materials were allowed to cool slowly. By 1937, Hershey claimed to have produced fifty synthetic diamonds ranging in size from microscopic to $2 \times 1.5 \times 1$ mm.

The tests used to prove that diamond formation had actually taken place were many and varied. The ultimate test now, of course, is subjecting the material to x-ray analysis, but unfortunately, this test couldn't be (or wasn't in later reports) used for identification at the time of formation.

Hannay turned his products over to Professor J. Storey Maskelyne who stated that, beyond doubt, they were diamonds. His tests involved lustre, lamellar structure on the surface of cleavage, refractive power, near inertness in polarized light, hardness, angle between cleavage faces and ignition products.⁵ Bannister and Lonsdale recently retrieved the specimens from the London Museum and proved that eleven of the twelve remaining were definitely diamonds according to Laue and powder x-ray patterns of them.

Moissan and Hershey used the same types of tests that Maskelyne used with positive results, but, again, these tests haven't been accepted as conclusive. In an effort to prove the authenticity of Hershey's work, a recent effort was made to have his products x-rayed. The main objection to accepting results of these recent tests lies in the elapsed time in which natural diamonds may have found their way into the artificial diamond collection.

The most vigorous objections to accepting the possibility that synthetic diamonds have been made naturally come from the investigators who have unsuccessfully undertaken the problem with an attack of their own or one based on reportedly successful results.^{4,7,8}

It is difficult to dismiss their findings by observing that the vast majority of the experiments carried on by the "successful" workers resulted in failure. At the present time, therefore, it is impossible to state without hesitancy that the production of a synthetic diamond has been accomplished. Theoretical calculations, however, indicate that the synthesis is indeed possible and much effort is now being spent in attempting to prove this beyond doubt.

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TRITIUM AS AN INVESTIGATIVE TOOL

D. Lierle

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Preparation

Tritium was first prepared by means of the $^2\text{H}(\text{d}, \text{p})^3\text{H}$ reaction.¹ Other means of production are now available. At the present time, most tritium is made by means of a $\text{Be}(\text{d}, 2\alpha)^3\text{H}$ reaction in a cyclotron; this reaction being common since cyclotrons almost invariably have beryllium targets. The $^2\text{H}(\text{d}, \text{p})^3\text{H}$ reaction affords a higher per cent yield, but the technical difficulties of preparing the target material are such as to discourage its use. By dissolving the target from the $^9\text{Be}(\text{d}, 2\alpha)^3\text{H}$ method in hydrochloric acid in a vacuum, and burning the evolved hydrogen isotopes over CuO , HTO is obtained and is collected in a liquid air trap. Some of the tritium originally made is occluded on the surfaces of the cyclotron, and combines with like-wise occluded deuterium to form deuterium tritride, DT , which diffuses through the fore vacuum line and is recoverable in the form of water via CuO .

A third mode of production of tritium is possible if strong neutron sources are available, as in a uranium pile reactor, by means of a $^6\text{Li}(\text{n}, \alpha)^3\text{H}$ reaction.² A fourth source would be the $^3\text{H}(\text{N}, \gamma)^3\text{H}$ reaction, resulting from the bombarding of the water cooling of the pile; however, this fourth method has not yet been tried.

From the crude tritiated water, the purification of tritium is relatively simple. It may be recovered either as HT or DT by electrolysis and collection of the cathode gas, which is then used for further synthetic purposes.⁴ As would be expected, the last fractions of the electrolyzed tritiated water contains the highest amounts of tritium.

Properties

Tritium is a negative beta emitter; it does not give off gamma radiation. Its radiation energy is the lowest found among artificially radioactive elements, 0.0179 Mev⁵. It has a half-life of 31 years. (It is to be noted that of artificially radioactive elements, nearly all having half-lives greater than a few weeks have radiations so soft as to require special detection procedures, e.g. T , ^{14}C , ^{35}S)⁶.

The vapor pressure of pure tritium is much lower than that of either protium or deuterium. For example, at 20.4°K, H_2 has a vapor pressure of 760 mm Hg., D_2 a vapor pressure of 256 mm., and T_2 (extrap.) a vapor pressure of 45±10 mm.⁷

Jones⁸ has calculated several thermodynamical functions for T_2 and TH from 0-2500°K, as well as ortho and para distribution of T_2 and the effect of the radioactivity of T_2 upon the attainment of thermodynamic equilibrium.

Measurement of the Radioactivity of Tritium or Its Compounds

(Up to the present time, the very great majority of reactions or topics investigated with deuterium or tritium as a tool have been organic or biochemical in nature.⁹ However, there is no reason for supposing that important advances will not be made in inorganic chemistry by their aid.)

As previously noted, the assay of tritium requires special treatment. For general measurement purposes the Geiger-Müller counter is employed. Because of the low energy of its beta-rays (hence a low range of the order of 1 cm. in helium at atm. pressure¹⁰), the tritium, in whatever form it is measured, must be introduced into the G-M counter in the gaseous state. However, the assay of tritium offers relatively little more difficulty than the assay of deuterium samples by the mass spectrometer.¹¹

The activity of tritium has been measured in the G-M counter as active butane,¹² active water vapor plus propane vapor¹³, active hydrogen plus ethanol vapor¹⁴, argon often being added. The counter behavior, of course, is influenced by the composition as well as the partial pressure of the constituents of the gas, as well as the volume of the counter.¹⁵

HTO vapor plus ethanol vapor, sometimes with argon, is often used for the counting gas. However, it is pointed out that counting characteristics of the G-M tube are better with hydrogen than most hydrogen-containing vapors; moreover, too great a partial pressure of water vapor results in spurious counts.¹⁶ Another disadvantage with water vapor is the gassing problem, i.e., the water is retained in the counter, giving "memory" effects.

Good results are reported from a study¹⁷ on an active hydrogen-ethanol-argon gaseous mixture as counting gas, the loss in reproducibility being less than 1%. In the range of partial pressures of HT studied (10-25 mm Hg.) the counting rate is proportional to the partial pressure of the active hydrogen sample.

Regardless of the form of tritium used, it is necessary after each activity determination to flush out "memory" effects by means of an inactive gas or vapor. The normal background of the G-M counter is determined by using a counter gas of the same composition originally used, protium being substituted for tritium.

Some miscellaneous factors affecting the error in measurement of the activity of the tritium in a G-M counter are the following:¹⁸

1. A large sample of the same specific activity, for the same amount of counting time gives a smaller statistical error than a small sample.
2. The detection efficiency for the beta particles decreases with increasing size, because of non-initiating disintegrations far from the central wire of the counter.
3. The G-M tube threshold and counting voltage can be appreciably diminished by decreasing the central wire diameter, for a given counter size and gas.

Syntheses of Organic Molecules Containing Tritium

Many syntheses have been published for putting deuterium in a given position in an organic molecule, as well as a smaller number for inorganic molecules, demonstrating the great utility of deuterium as an investigative tool. The general methods for organic syntheses are;

1. An exchange reaction between the organic compound and some deuterio-compound.
2. A chemical synthesis for introducing the deuterium.
3. A biosynthetical means of deuterium introduction.

Because of the small available amount of tritium available until now, it has not been used as often as a labeling agent as has deuterium. However, it is not improbable that the deuterio-labeling techniques will apply for tritium. Tritium and deuterium, in all cases where compared, parallel each other closely in their respective exchange characteristics.¹⁹

Tritium as an Investigative Tool (General Considerations)

One would expect that tritium would behave somewhat differently from protium, due to the greater mass of the former. This is correct. Isotopes are not functionally identical entities, as exemplified most strongly by the hydrogen isotopes. The hydrogen atom is the only chemical element which can be found as a bare nucleus. The difference in mass between tritium and protium is of the order of 300%. Other element isotopes are not nearly even 100%.

If we consider the difference in the hydrogen isotopes with respect to bonding, we find that the C-¹H bond is weaker than the C-²H, which in turn is weaker than the C-³H. This difference is due to the difference in zero point energies of the isotopes. The lightest isotope has the highest zero point energy, the vibrational energy resident in the chemical bond at 0°K, and the predominant contributor to the total internal energy of binding at ordinary temperatures. By the quantum theory, the energy of vibration is equal to Planck's constant h , multiplied by a characteristic vibration frequency, which is an inverse function of the effective mass of the oscillating atoms. Therefore, an increase in the mass of an isotope results in a smaller zero point energy, and a consequently higher activation energy. Thus, we would expect tritium to be more inert with regard to reactions involving transfer of the isotope from carbon to carbon, which is the case experienced. As an example of a molecule which is very responsive to the differential in energy of activation of a C-H bond, we have hydrogen-transporting enzymes. It is possible that selective reactions could occur in enzyme-catalyzed reactions, invalidating tritium as a tracer. We would expect it by analogy with deuterium, which effectively slows the oxidation of glucose, an enzymic hydrogen exchange reaction.

Bigeleisen²⁰ has given an interesting mathematical consideration of the variation of the exchange rate of a given reaction for

the isotopes of an element. He estimates that the specific reaction rate constant for deuterium is 18 times as great as for protium, and for tritium 60 times as great as for protium.

It is evident that there is generally an uncertainty factor in the use of tritium as a tracer for hydrogen, and that much care must be exercised for ruling out isotope effects, wherever it is possible for them to enter.

After having seen the difficulty attending the tracer use of tritium, it would be fitting to mention some of the advantages of using tritium, which are:

1. Great dilution ranges are possible with tritium and its compounds; a dilution ratio of 10^7 - 10^8 is possible from 1 cc. of a 5-10 cc. sample of tritiated water with a total activity of 10^{10} - 10^{11} ct/m, which sample is available.²¹
2. When wishing to conduct a biochemical tracer experiment, it is usually much easier to synthesize the pertinent compound containing deuterium than containing radioactive carbon.²² We would expect the same to be true for tritium.
3. In view of the great dilution ranges possible, and the very low energy of the tritium beta-particles, it offers great possibilities in studies on living matter, where radiation damage could be a limiting factor.²³
4. It is possible that a compound needing labeling in a specific position, e.g., on N or O, can be labeled with tritium, when the labeling with deuterium would be useless. For example, deuterium can't be stably combined in $-NH_2$ or $-OH$, because in aq. media, enough dissociation occurs that fast equilibration results between the group and the water or other labile hydrogen present. Such deuterio-compounds have little importance for tracer work.²⁴
5. Tritium is a good auxiliary labeling agent for carbon, because of the stability of its linkage with carbon.

Experiments Utilizing Tritium

For the purpose of illustrating the uncertainties arising from the tracer use of tritium, and methods used to eliminate this uncertainty, the study of Norris et al²⁵ on chlorophyll in photosynthesis has been used. Prevailing theories on the role of chlorophyll are of two types; 1) It acts as a reducing agent; 2) It acts merely as a sensitizer of chemical bonds. The experimenters endeavored to check the validity of theories based on 1). They reasoned that if photosynthesis is allowed to proceed for a sufficient length of time in a solution of tritiated water, chlorophyll-hydrogen atoms involved in the redox cycle would be replaced by tritium.

The experiment was carried out on green algae suspended in a bicarbonate solution containing HTO, subjected to strong light. It was calculated that each chlorophyll molecule must have participated in 100 redox cycles. The chlorophyll was removed, subjected to various purifications (in the dark), and the activity finally measured in a G-M counter as hydrogen. The activity of the hydrogen was always undetectable. The experimenters cited two objections to the conclusion that chlorophyll did not react in a hydrogen transfer reaction: 1) Thermal exchange during purification has resulted in a loss of tritium, 2) Isotopic separation occurred so tritium didn't participate in protium reactions.

The first objection was met by preparing pure chlorophyll, suspending it in tritiated water and exposing it to light. The detectable activity was so small as to lead to the conclusion that the chlorophyll contained no thermally exchangeable hydrogen.

Objection 2) could not be met successfully; it was concluded from the experiment that either isotopic separation occurred or that chlorophyll was not a reducing agent. The experimenters stated that use of 100% D₂O would circumvent isotopic separation and yield an unequivocal conclusion.

Tritiated water has been used to determine the total body water of human beings²⁶, the method being based on the assumption that no other exchange reactions occur within the body. The tritiated water is injected and the total body water calculated from the simple formula $A_1 V_1 = A_2 V_2$, where A_1 is the activity in the volume V_1 of injected stock solution; A_2 the activity of the volume V_2 of the body fluid measured, e.g., plasma, after exchange equilibrium between the body and tritiated water is attained.

A method of measuring the solubility of water in liquid hydrocarbons via DTO has been developed²⁷, such solubility having been determined only for benzene, toluene, cyclohexane, and various gasolines and oils. Briefly, the method consists in the operations: 1) saturation of the hydrocarbon with DTO at the desired temperature by bubbling air saturated with DTO. 2) Taking an aliquot portion of the saturated solution, 3) Measurement of the aliquot's activity, from which the solubility is calculated.

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THE NITRONIUM ION AND SOME NITRONIUM COMPOUNDS

Melvin Tecotzky

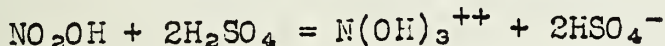
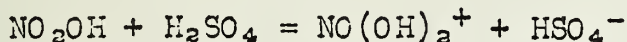
January 18, 1951

Evidence For The Existence of NO_2^+

Solutions of nitric acid have been widely investigated because of their nitrating properties. The first suggestion that the nitronium ion may be the active nitrating agent was made by Euler in 1903.(3) Physical measurements of solutions of nitric acid in concentrated and aqueous sulfuric acid solutions have led investigators to report that reversible hydration and dehydration of nitric acid take place in these solutions (15), the end product of the dehydration process being nitrogen pentoxide. It was further suggested that the presence of nitrogen pentoxide in the sulfuric acid solution resulted in a totally different ultra violet absorption spectrum for anhydrous nitric acid and its solutions in sulfuric acid (7).

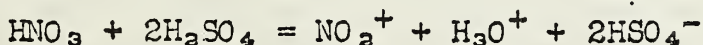
The Raman spectra of nitric acid in sulfuric acid contain two lines, one at 1050 cm^{-1} and the other at 1400 cm^{-1} . These lines cannot be attributed to either of the acid molecules. (12,1). The spectra of solutions of nitrogen pentoxide in nitric acid also contain lines at approximately 1050 cm^{-1} and 1400 cm^{-1} . These lines increase in intensity with increasing concentration of nitrogen pentoxide.

Hantzsch believed that a solution of nitric acid in sulfuric acid would react as follows:

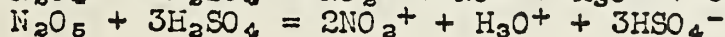
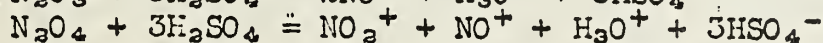


He reported that nitric acid produced a three fold depression of the freezing point of sulfuric acid (8). This evidence, plus a study of the ultraviolet absorption spectrum of sulfuric acid solutions of nitric acid (9), convinced Hantzsch that the ion present in solution is H_2NO_3^+ or $\text{H}_3\text{NO}_3^{++}$. Since he was unsuccessful in isolating $(\text{H}_2\text{NO}_3^+)(\text{HSO}_4^-)$ or $(\text{H}_3\text{NO}_3^{++})(\text{HSO}_4^-)_2$, Hantzsch was unable to support his claims.

Recently strong evidence has been obtained indicating the existence of the nitronium ion (NO_2^+) in these solutions.(4). The investigators repeated Hantzsch's cryoscopic work. It was established that the freezing point depression produced by nitric acid in sulfuric acid is four fold. This has been taken to indicate that the nitronium ion is formed in the solution according to the following equation:

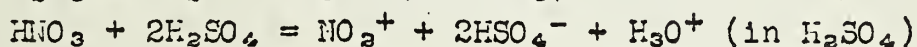
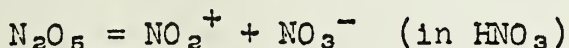


It was also reported that nitrogen trioxide, tetroxide, and pentoxide all produce six fold depressions of the freezing point of sulfuric acid. The equations for these reactions are:



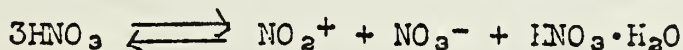
Raman spectroscopy was used to prove the existence of the ions above in the various solutions. (H_3O^+ is an exception; it cannot be detected in this manner).

An interpretation of the Raman spectra of solutions of nitric acid in sulfuric acid and nitrogen pentoxide in nitric acid has been offered. The Raman spectra of these solutions contain two frequencies, one at 1050 cm.^{-1} and the other at 1400 cm.^{-1} in addition to the frequencies of the acid molecules. By comparing the nitronium ion with molecules such as CO_2 and N_2 , which have the same symmetry, it has been concluded that the Raman spectrum of the nitronium ion should consist of only one line with a frequency a little greater than 1320 cm.^{-1} . Of the two frequencies found by Chedin (2) 1400 cm.^{-1} and 1050 cm.^{-1} , the former has been attributed to the NO_2^+ molecule. The other frequency has been attributed to the nitrate ion in solutions of nitrogen pentoxide in nitric acid; and to the bisulfate ion in solutions of nitric acid in sulfuric acid. Odd as it may seem, these two ions both possess strong frequencies at about 1050 cm.^{-1} . This observation of the lines at 1050 cm. and 1400 cm. in the spectra of these solutions is consistent with the following ionizations:



The interpretation of the spectra given above has been verified by an investigation of the Raman spectra of mixtures of nitric acid with other strong acids (11). It has been found that the Raman spectra of mixtures of nitric acid with either selenic or perchloric acid contain an intense line at about 1400 cm.^{-1} , but no trace of the line at 1050 cm.^{-1} . Instead, lines corresponding to the perchlorate or biselenate ion were found to be present. These results are taken to indicate that the frequencies 1400 cm.^{-1} and 1050 cm.^{-1} originate from different molecular sources.

From the experiments it has been concluded that nitric acid when mixed with a stronger acid yields the anion corresponding to the stronger acid and some other ion whose Raman spectrum consists of one strong polarized line with a frequency of approximately 1400 cm.^{-1} . The nitronium ion is the only possible entity in the solutions which satisfies the conditions. Thus it is evident that Raman spectroscopy provides evidence of identity as well as a convenient method for the detection of the nitronium ion. Raman spectra have also shown (14) anhydrous nitric acid undergoes self dissociation to yield nitronium ions. The equation proposed is:



Cryoscopic measurements indicate that the concentration of nitronium ion in anhydrous nitric acid is about 1% by weight (5).

THE CHEMISTRY OF NITRONIUM SALTS

An attempt was made to isolate some salts of the nitronium ion (6). The nitronium salt (NO_2^+) (X^-) has been regarded as the ionized form of the mixed anhydride of HNO_3 and HX . If HX is a very weak acid such as water, or a moderately weak acid such as

benzoic, the mixed anhydride HO_2K is completely covalent. Solid nitrogen pentoxide is nitronium nitrate (NO_2^+) (NO_3^-). (11) In the gaseous form it has a covalent structure. These facts lead to the conclusion that stable nitronium salts would be produced only with the anions of acids which are at least as strong as nitric acid. Several nitronium salts with such anions have been prepared (6).

Hantzsch (10) has reported the preparation of two salts by the reaction of nitric acid with perchloric acid. The British investigators could not repeat his work, but have prepared some nitronium salts. Nitronium perchlorate (NO_2^+) (ClO_4^-) has now been prepared (6). The salt forms colorless crystals and decomposes without exploding above 135°C . giving off nitrogen dioxide. Nitronium hydrogen pyrosulfate (NO_2^+) (HS_2O_7^-) has been obtained by treating nitric acid with sulfur trioxide in nitromethane solution. Nitronium pyrosulfate (NO_2^+)₂($\text{S}_2\text{O}_7^{2-}$) has also been prepared through the use of smaller quantities of sulfur trioxide. Both of these compounds form colorless crystals. Using larger molecular proportions of sulfur trioxide, it was possible to prepare nitronium trisulfate (NO_2^+)₂($\text{S}_3\text{O}_{10}^{2-}$). Through the reaction of nitrogen pentoxide and fluorosulfonic acid, nitronium fluorosulfonate (NO_2^+) (FSO_3^-) was prepared. Evidence for the existence of these salts has been obtained by analysis and by the use of Raman spectroscopy (13).

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The Structures and Properties of Some Metallic Derivatives of Dyes

Jennie C. Liu

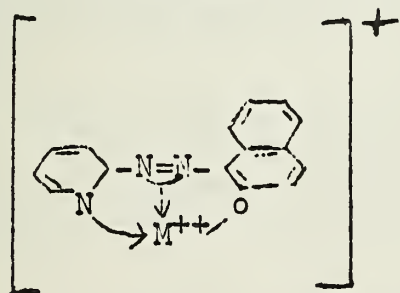
February 13, 1951

I. Azo Dyes

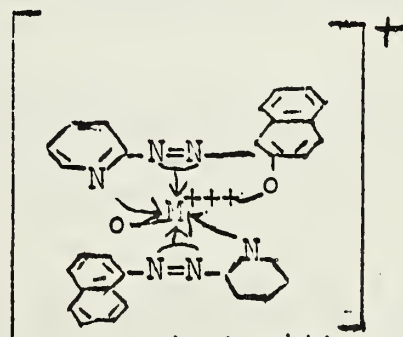
Previous investigation has shown definitely that lake formation with metals increases the stability of the azo dyes, particularly toward light and washing. The stability of the lake, as well as that of the dye itself, is enhanced by inner coordination of the metal with the azo nitrogen; such forms arise only when the metal is affixed by covalent linkage to substituents eg. OH, COOH, NH₂ etc. ortho to the azo linkage. Consequently the presence of two substituents of this kind in the o, o' positions further increases the stability of the lake which assumes a fused ring formation. Meta or para substituents have no effect.

Generally, the metal combines with the dye molecule by replacing the hydrogen atom from the hydroxy or carboxy group and accepting an electron pair donated by an oxygen or a nitrogen atom. The chelate ring thus formed consists of five or six members which is in the most stable form. Due to the fact that nitrogen in the pyridine ring possesses an unshared electron pair, it would be expected that α -pyridyl azo compounds would donate an additional covalent bond through the pyridyl nitrogen to the metal. Hence an investigation of some lakes of α -pyridyl azo derivatives of β -naphthol and resorcinol was undertaken.

With α -pyridyl azo β -naphthol, the divalent metallic lakes, like those of copper (II) and nickel (II) were found to contain one azo residue to one metallic atom, the second valency of the metal remaining associated with an acidic radical (form I). In the case of trivalent metallic lakes, like those of chromium, cobalt and iron, dye: metal complexes in the ratio 2:1, were formed. (form II)



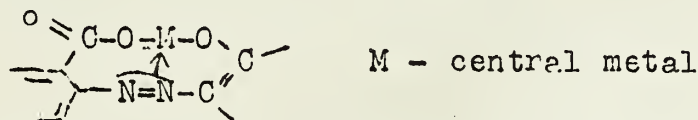
M⁺⁺ - divalent metal (I)



(II) M⁺⁺⁺ - trivalent metal

The presence of an additional hydroxy group para to the azo linkage as in the case of α -pyridyl azo resorcinol gives water soluble lakes of similar type with an additional primary valence of the metal satisfied by replacement of the hydrogen ion from the incoming acid group.

A study of some lakes of α -[o-carboxy azo benzene]-o'-chloro-acetonacetanilide and α '-carboxy-benzene-4-azo-1-phenyl-3-methyl pyrazol-5-one has been made to extend further the knowledge of the azo lakes. After enolization these two o-carboxy-azo-o'-ketonyl dyes are structurally similar to the o-carboxy-azo-o'-hydroxy compounds. Two five or six membered chelate rings would be formed as follows:



Spectrophotometric determination and magnetic measurement have been used in some cases to study further the structures and properties of the lakes.

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II. Substituted 8-hydroxyquinolines

Although methods involving the use of 8-hydroxyquinoline (or oxine) as a quantitative precipitant have been extensively investigated and widely used, little information can be obtained from the structural point of view. Since polar group e.g. OH^- , COOH^- or SO_3H^- para to the point of coupling on the aromatic nucleus has remained completely independent to the coordination sphere and acts merely as the solubility promoting vehicle, an investigation involving the structural and stereochemical study of the substituted 8-hydroxyquinoline in comparison with the parent substance was undertaken. The particular derivative chosen for this work was 8-hydroxyquinoline-5-sulfonic acid.

Cadmium and zinc sulfonyl oxinates were prepared and found to be fluorescent in aqueous medium as well as cadmium and zinc oxinates in chloroform. Spectrophotometric determination indicated that a 2:1 dye: nickel complex is formed in aqueous solution.

A conclusive proof that the zinc complex has a tetrahedral configuration would lie in the resolution of this salt into its optically active isomers. Strychnine was found to be a satisfactory resolving agent. From the rotation data obtained, partial racemization was accomplished, but in no case did the separation of isomers seem to be complete.

Since nickel and cupric complexes of sulfonyl oxime are expected to be planar in structure, an attempt to separate these into their geometrical isomers was made. So far, attempts to achieve this objective have been unsuccessful.

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STUDIES IN PHOSPHORUS CHEMISTRY

John R. Mills

February 27, 1951

A. Introduction

Many of the important reactions in the field of phosphate chemistry occur in the fused or solid state at relatively elevated temperatures. Dehydration reactions, condensation reactions in which discrete PO_4 tetrahedra combine to form polyanionic aggregates, or the reverse depolymerization processes, may be cited as examples. The present investigation covers to a large extent the study of such high temperature reactions, utilizing certain techniques which are especially adaptable to such systems.

B. Differential Thermal Analysis

This technique consists essentially of measuring the temperature difference between the sample under study and a sample of aluminum oxide, which undergoes no transformation accompanied by heat effects over the useful temperature range, while both are heated at a controlled rate. Any heat effect due to a change in an unknown sample is immediately reflected by a difference in temperature between the sample and aluminum oxide, an exothermic reaction by a positive algebraic difference and an endothermic reaction by a negative difference. The sample temperature is synchronously recorded, so that a comparison with the differential plot enables a determination of the temperature at which a reaction begins and ends.

X-ray diffraction analysis of the reaction products was also used extensively

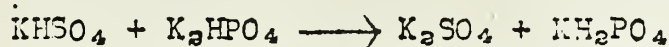
C. Alkali Metal Sulfate-Phosphate Systems

Considerable similarity in structural chemistry exists between silicates and phosphates, due primarily to the fact that the basic structural units are SiO_4 and PO_4 tetrahedra. Similar chain, ring and three dimensional polymers are known in both the phosphate and silicate systems. There is evidence that these similarities extend to other elements as well. Thus B, S, Mo, W, Te, Cr, and V all form pyro-ions. The possibility of forming compounds of mixed structure, for instance pyro-ions having a composition $\text{O}_x\text{-A-O-B-O}_y$, where A and B are different elements of the above series would seem feasible. Recently a complex meta arsenato-phosphate has been prepared (1) and the formation of mixed pyro- compounds of sulfur and phosphorus, Na_3PSO_7 , KNa_3PSO_7 has been reported (2). A number of references to such complex phosphorus-sulfur compounds are made in the earlier literature of inorganic chemistry (3,4,5), and so it was decided to check on their existence, and if possible to prepare others of this type. It may be noted that the P-O and S-O bond distances in the PO_4 and SO_4 tetrahedra are very similar. 1.55 Å, and 1.51 Å respectively.

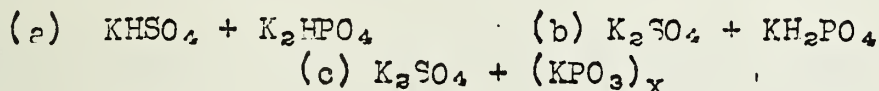
1. The Reaction of KHSO_4 with K_2HPO_4

Poni and Cernatescu believed that they had prepared Na_3PSO_7 and KNa_2PSO_7 by an intermolecular dehydration of NaHSO_4 or KHSO_4 and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ at a temperature

$\text{NaHSO}_4 + \text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} \longrightarrow \text{Na}_3\text{PSO}_7 + 3\text{H}_2\text{O}$
just above the fusion point of the mixture. Since theoretically such compound formation is favored by a larger cation a preliminary examination of the corresponding potassium system was conducted. Differential thermal analyses, together with X-ray diffraction analysis of the products indicated a new type of high temperature acid-base reaction was actually taking place.



This reaction is strongly exothermic and occurs at 180°-200°C.; just below the melting-point of KHSO_4 (210°C.). Dehydration for 24 hours at a temperature as low as 210°C. showed a weight loss corresponding to the removal of one mole of water for each mole of reagent, and a change in the X-ray diffraction pattern indicating the disappearance of KH_2PO_4 and the formation of KPO_3 . Apparently the normal dehydration of KH_2PO_4 to $(\text{KPO}_3)_x$ proceeds in the presence of K_2SO_4 which remains inert. A further check on this hypothesis was made by heating the following three mixtures to fusion, cooling, and comparing the X-ray diffraction patterns and $(\text{KPO}_3)_x$ content of each.



All three sets of reagents showed the same eutectic break at about 750°C., were completely molten at 950°C. and displayed an endothermic reaction at 588°C. corresponding to the transition of K_2SO_4 from orthorhombic to hexagonal form. Mixture (a) revealed a strong exothermic reaction commencing at 180°C., not shown by (b) or (c), and both (a) and (b) showed breaks in the neighborhood of 275°C. corresponding to the rapid dehydration of KH_2PO_4 to KPO_3 . The X-ray diffraction patterns of the products were identical for all three mixtures, and the lines corresponded to a simple eutectic mixture of K_2SO_4 and $(\text{KPO}_3)_x$. Chemical analysis showed the following KPO_3 contents.

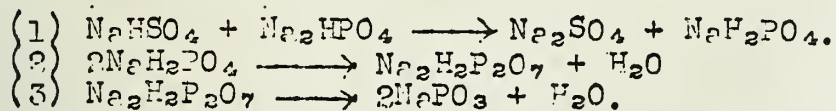
Mixture	% KPO_3 (water soluble)	%Water soluble phosphorus is KPO_3	Total	Theoretical
(a)	36.2	5.1	41.3	40.4
(b)	36.9	4.34	41.2	40.4
	37.0	4.35	41.3	40.4
(c)	35.2	5.3	40.5	40.4
	35.1			

Due to the high melting point of K_2SO_4 it was not possible to determine the phase diagram for the KPO_3 - K_2SO_4 system with the

present apparatus, but it seems apparent from the above that no compound K_2PSO_7 can be formed by thermal means.

2. The Reaction of $NaHSO_4$ with Na_2HPO_4 .

A corresponding study of the sodium system revealed that essentially the same type of reactions were involved. In this case however the intermediate formation of $Na_2H_2P_2O_7$ upon dehydration of NaH_2PO_4 was noted. The reactions may be summarized by the following equations



A phase study of the $(NaPO_3)_x - Na_2SO_4$ system revealed only a simple eutectic system with no compound formation.

The acid-base reaction (1), although not as exothermic as in the case of the potassium system, commences at $145^\circ C$.

A weight loss corresponding to the theoretical water loss for equation (2) was found at $200^\circ C$. It has already been shown that NaH_2PO_4 yields $Na_2H_2P_2O_7$ rapidly at this temperature. X-ray diffraction patterns gave good evidence for this transition and an analysis for pyrophosphate showed 25.0% by weight of pyrophosphate calculated as P_2O_5 compared with a theoretical 28.0%.

As a further check on the course of these reactions differential thermal analysis of the mixtures $NaHSO_4 + Na_2HPO_4$; $Na_2SO_4 + NaH_2PO_4$; $Na_2SO_4 + \frac{1}{2} Na_2H_2P_2O_7$; and $Na_2SO_4 + (NaPO_3)_x$ were conducted, and as before these showed a stepwise elimination of certain heat effects. The final fusion point was the same in all cases ($795^\circ C$.) as were the X-ray diffraction patterns of the cooled samples. The products show lines corresponding to the high-temperature hexagonal form of Na_2SO_4 (transition $240^\circ C$.) Certain qualitative chemical tests on the product agreed with those obtained by Poni and Cernatescu, which together with the above evidence leads us to conclude that no compound is formed.

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FLUORINE TECHNOLOGY

Roger W. Sanftner

March 6, 1951

There is little general appreciation of the work required to place a chemical into full-scale production once the basic synthesis has been developed. A mere million-fold increase of a recipe involves more than the buying of a larger capacity pump or the use of a larger pipe size to handle the quantities required. Negligible heat effects in laboratory synthesis could conceivably result in insurmountable heat exchange problems in production, while a slight film in the test tube might deposit in equipment so badly as to require replacement of a unit in a short time. The resolution of technological process requires careful analysis for the most practical and economic solution. Rarely are new and revolutionary concepts required, but rather rather simple concepts applied logically and consistently. The development of production methods for fluorine is a particularly good example. Fluorine production at the outset presented a seemingly impossible problem, but painstaking research led to the production of what has been termed in A.E.C. papers to be "huge amounts of fluorine" (3).

The present method of producing fluorine is basically that used in its discovery, namely the electrolysis of a fused potassium fluoride-hydrogen fluoride. Three general types of cells have been developed: (a) low temperature, $\text{KF} \cdot 3\text{-}4\text{HF}$ ($60^\circ\text{C}.$); (b) medium temperature, $\text{KF} \cdot 1.8\text{-}2.0 \text{ HF}$ ($90^\circ - 110^\circ\text{C}.$); (c) high temperature, $\text{KF} \cdot \text{HF}$ (250°). The early cells were characterized by high corrosion, low efficiency, and intermittent operation.

The considerations which were required before the overall problem could be undertaken were: (a) choice of an electrolyte; this in itself dictated the materials of construction and operating temperature; (b) mechanical design of the cell and its auxiliary equipment; (c) disposal of the fluorine and the by-products; (d) storage and transportation.

The choice of the medium temperature type of cell was made primarily in an attempt to compromise the disadvantages of the low and high temperature type cells and to incorporate as many of their advantages as possible. It permitted among other things, the use of steel in construction, the employment of an easily attained and easily maintained operating temperature, and the use of carbon electrodes.

Little information was available concerning the structural capabilities of various materials under the conditions of operation. It could be assumed, however, that certain parts of the cell would require frequent replacement. Cost considerations demanded rapid and cheap replacement of electrodes and other cell units. The choice of a proper material for use as the anode presented

many difficulties. The criteria taken as characteristic of an ideal anode were: (a) good conductivity, (b) ease of connection electrically, (c) low corrosion, (d) high physical strength, (e) ease of fabrication (f) operation in an electrolyte containing traces of water, (g) high current efficiency, (h) density great enough to allow the anode to sink in the electrolyte if breakage occurred (16).

Nickel possesses the best properties of any metal, but when it is used in a medium temperature cell operating at 100°C ., approximately 10% of the current is consumed in converting nickel to NiF_2 which forms a finely divided solid suspension in the electrolyte and finally forms so much sludge that the cell will not operate. Nickel anodes are used extensively, however, because they will operate in the presence of water. They are thus used to condition the electrolyte.

In a search for anodes which would not foul the electrolyte and would have better current efficiency, several types of carbon were studied. Graphite was found to operate satisfactorily for a short time, but it was subject to swelling which resulted in breakage and loss of electrical contact. It was found that hard ungraphitized carbon rods were suitable in this respect, but were subject to breakage, and failed to operate in a wet electrolyte. The low specific gravity resulted in floating of the broken part which then shorted the cell. The most serious objection to carbon anodes was that of the difficulty in making electrical contact. This resulted in polarization which could be eliminated only by anode replacement. Copper impregnated carbon anodes were developed to eliminate these disadvantages.

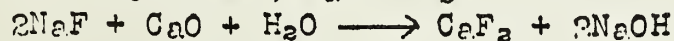
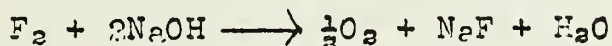
The electrolyte can be prepared by passing HF gas into molten KHF_2 until the proper mole fraction is obtained. During the electrolysis HF is lost and must be replaced. A smoother cell operation is obtained when the acid is added continuously. Since this required considerable personal attention as well as a scheme for measuring the total HF flow to each cell, a batchwise procedure was developed. After preliminary electrolysis to remove impurities from the electrolyte, the nickel anodes are replaced by carbon. The cathode and anode spaces are flushed with nitrogen and the current is brought to its full value.

Fluorine can be conducted in standard steel pipes or in copper tubings. Welded construction is preferable to flanged or screw piping at any pressure. Monel pipe should be used with fluorine under pressure. Because of the abrading action encountered in turning a valve, materials such as nickel or monel which show a minimum scale formation should be used. The development of satisfactory instruments is of course limited by the reactivity of fluorine. Satisfactory gages have been developed, but no satisfactory pressure relief valves have been made because of seat leakage. For operations with fluorine under pressure, control is best obtained by using several valves in series with suitable alarms and by-passes.

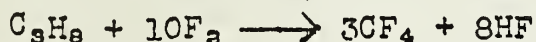
In order to maintain continuous operation, storage and disposal facilities must be provided. Should cell shut-down be necessary, enough fluorine must be provided to keep dependent processes in operation. The storage of fluorine presents a great hazard, especially where large quantities are involved. For maximum safety only nickel or monel of adequate thickness should be used in contact with fluorine under pressure. The containers should be isolated in concrete rooms adequately ventilated and made largely inaccessible to the operator.

Should a fluorine consuming process be forced to shut-down, the disposal of fluorine is imperative. Even in low concentrations and mixed with HF, these gases are toxic and unpleasant, as well as destructive to crops as far away as 10 miles. The principle disposal processes are:

Reaction with caustic soda



Reaction with hydrocarbons



For its continued existence, a process is always subject to economic considerations. When new processes become more efficient, the older methods must be abandoned. Fluorine is no exception so it is now being relegated to a place of accomplishment and is being replaced technologically by processes such as anodic fluorination.

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March 13, 1951

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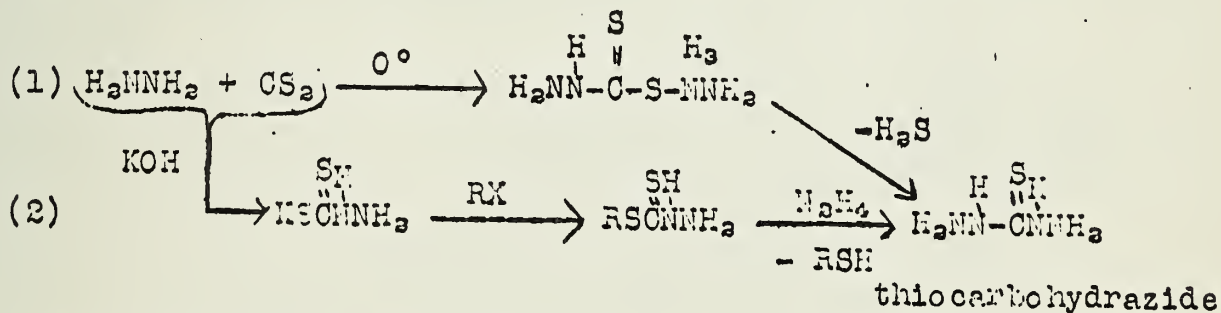
1) To gain a knowledge of the solvolytic and desolvation reactions by which they are prepared and the conditions necessary to bring about such reactions.

2) To determine the nature and extent of the complexing ability of these compounds, some of which are already employed as analytical reagents.

3) To produce compounds which exhibit useful biological activity. The evidence now available indicates that such compounds may be expected to show some physiological activity.

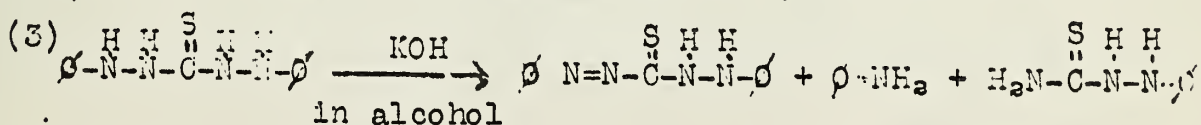
characteristic reactions employed in the synthesis of $\text{H}_2\text{N}_4\text{-CS}_2$ derivatives:

1) Direct attachment of a N-NH₂ group to carbon disulfide. The versatility of this reaction is indicated by the following equation

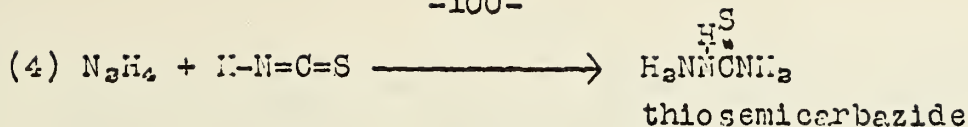


Other basic groups may also be employed in replacing the RS- group to give unsymmetrical products. Moreover the hydrazine derivative originally used may be varied considerably.

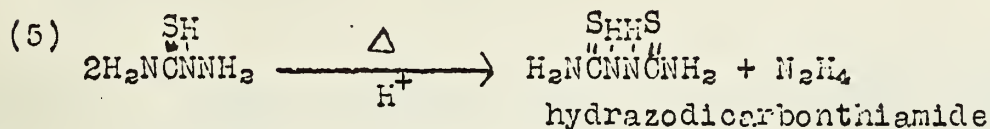
Dithizone (diphenylthiocarbazone) is prepared in an analogous fashion, the last step being an internal oxidation-reduction as shown by the following equation:



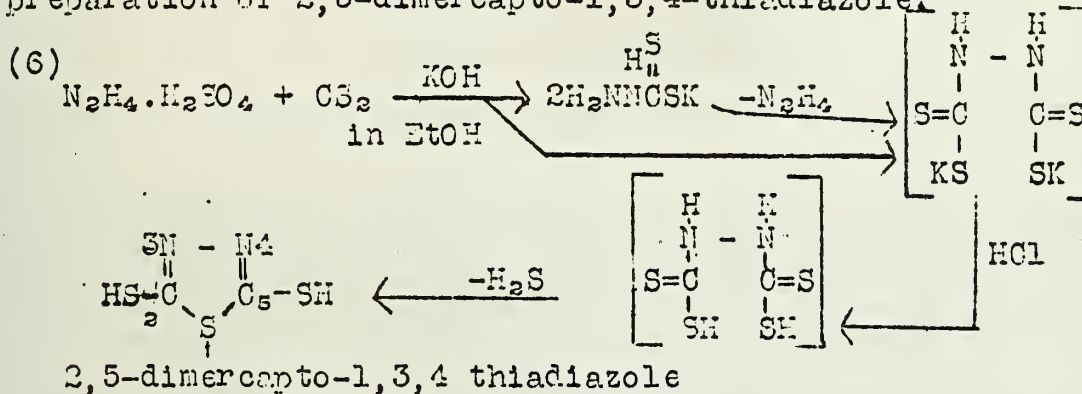
2) The "solvation" of thiocyanic acid by a hydrazine derivative to produce mixed ammono-hydrazino derivatives of carbon disulfide. This is best illustrated by the formation of thiosemicarbazide. Substituted hydrazines and isothiocyanates may be used to produce 1 and 4 substituted products.



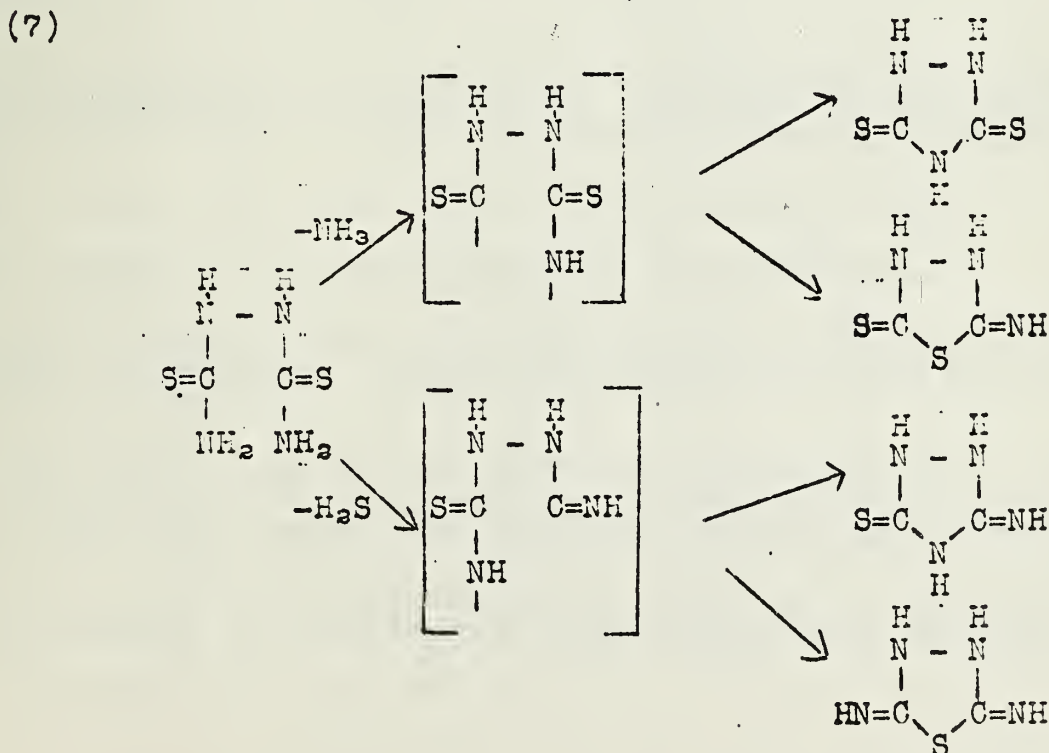
3) Desolvation of thiosemicarbazides to prepare straight chain compounds.



4) Desolvation accompanied by ring closure. A simple case where only one type of desolvation is possible is shown in the preparation of 2,5-dimercapto-1,3,4-thiadiazole. --



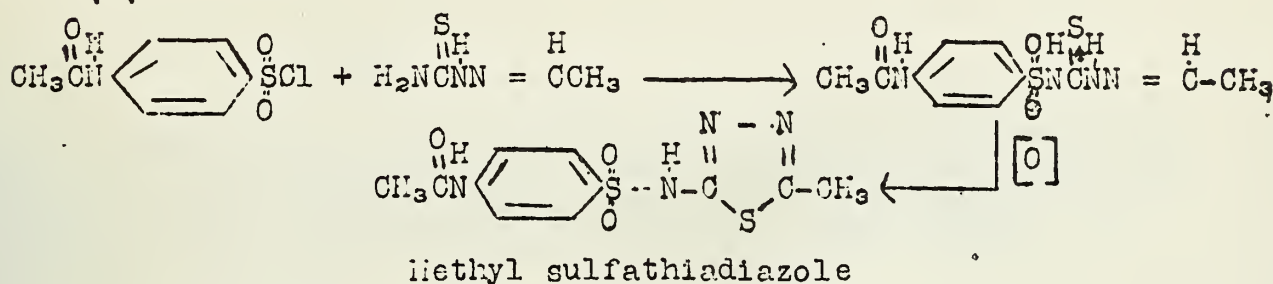
Where the compound of the diamide type is used ammonia or hydrogen sulfide may be eliminated and ring closure may occur through either the sulfur or nitrogen as shown in the following processes:



Substitution on the amide nitrogen or sulfur may influence the type of ring closure.

- 5) Oxidative ring closure. In some cases the mercapto groups may be oxidized to form an internal thio ether. Of more particular interest here is a case in which hydrogen is removed to close a ring resulting in the formation of sulfathiadiazole compounds.

(8)



Applications of Hydrazine-Carbon Disulfide Derivatives to Analytical Chemistry.

Examples are given below to illustrate the nature of the compounds formed and methods used in separating ions which may be applicable in the study of new compounds. The separation of cations through the use of dithizone has been studied extensively. This particular reagent is discussed to illustrate the principles involved.

Dithizone complexes a great many metal ions and precipitates them from aqueous solution. However, these dithizonates are soluble in carbon tetrachloride and chloroform and ionic separations are carried out by extracting the aqueous solutions with chloroform solutions of the reagent. Since dithizone complexes so many metals, special procedures are generally employed to facilitate the isolation of a single species.

1) Altering the pH: The formation of dithizonates is strongly dependent on hydrogen ion concentration. The order of extraction in going from a pH of 1 to 5, sodium hydroxide solutions is as follows:

Au, Pt, Pd, Ag, Hg, Sn^{++} , Cu^{++} , Bi, Zn, Co, Ni, Pb, Tl, Cd

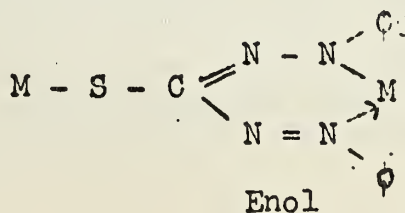
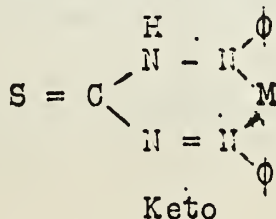
Separation normally is not accomplished in one extraction.

2) Introduction of other complexing agents to alter the ionic concentrations in solution. Cyanide and acetate have been particularly useful in this respect.

3) Alteration of the valence state of the metallic ion. This is of less importance than the preceding methods but may be of more importance with other reagents not so easily oxidized as dithizone.

According to Fischer, dithizone forms complexes in the keto and enol forms for which the following structures have been proposed:

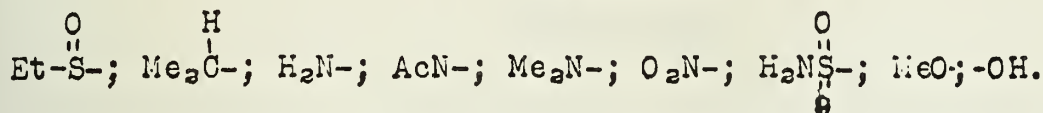
1) Monovalent ions



ring structures are obtained. These compounds proved to be quite effective and a tremendous amount of work has been reported concerning the preparation and evaluation of these materials. From this information, some generalizations may be made.

1) The thiosemicarbazones of aryl aldehydes are the most active. Alkyl derivatives have no or very low activity and aryl ketones are less active than aldehydes.

2) Substitution of a polar group para to the carbonyl function increases the activity. The groups found to be most effective are:

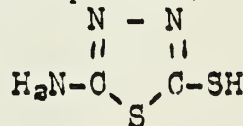


The amino or acetamido substituted compound is the one frequently employed and is referred to either as TB 1/ These compounds have some very particularly apparent in the treatment of advanced cases so should not be considered the ultimate in the treatment of tuberculosis but are very useful if properly employed.

One of the side reactions produced by Conteben treatment is the development of anemia. According to one author this anemia parallels a drop in the copper concentration of the blood of these patients. This has led to the hypothesis that the complexing of copper is the mechanism of activity. It is pointed out that p-aminosalicylic acid, 2-anilino-3-imino-5-phenylphenazine and Conteben all form stable copper complexes and are active therapeutics, whereas less active medicinals form less stable copper complexes. The author presents a good case but this theory does not explain the influence of para substituents. The idea that complexing trace elements may account for biological activity is becoming more widely accepted, but it is probable that more than one factor determines the specific activity of any compound.

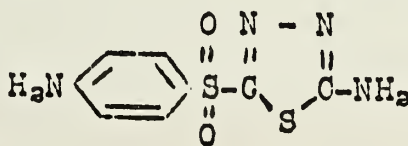
It is also reported that Conteben has a favorable effect in the treatment of some rheumatic conditions.

Some other useful cases of biological activity are reported. For instance, 5-amino-2-mercapto-1,3,4-thiadiazole



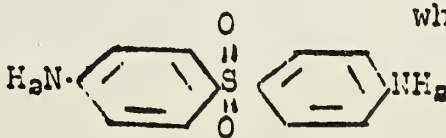
is reported to be a more active and less toxic antithyroid than thiouracil which has been used clinically. Clinical evaluation has not been completed as yet.

Sulfones of the type



are said to be

less toxic than the material



which is used in

leprosy treatment and show similar activity. Here again complete investigation of the problem is lacking.

Patents have recently been issued covering substituted thiadiazoles as paracitocides and fungicides while thiosemicarbazones of some aldehydes and ketones, some thiocarbonylhydrazides, and thiosemicarbazide are patented as insecticides. The evaluation of these materials is now in progress.

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THE STRUCTURE OF POLYSULFIDES AND POLYTHIONIC COMPOUNDS

William F. Ulrich

March 20, 1951

The exact structure of the polysulfide and polythionates is a problem which has received attention for a number of years. Even today there is a wide difference in opinion as to whether these substances are composed of linear or branched chains.

The evidence in favor of the latter concept is primarily chemical in nature, although some physical measurements have been interpreted in this respect. For example, Smyth and co-workers (1) measured the dielectric constants and densities of hydrogen disulfide and sulfur monochloride in benzene, and calculated the dipole moments of these molecules. On the basis of their data they proposed the structures $H_2S \rightarrow S$ and $Cl_2S \rightarrow S$.

The chemical behavior of ethylene tetrasulfide appears to support this structure, as two of the sulfur atoms react differently from the others. They may be removed from the tetrasulfide to produce the disulfide, and then replaced to reform the original material. Patrick (2) suggests that the $\begin{matrix} S & S \\ \uparrow & \uparrow \end{matrix}$ structure explains this better than an unbroken chain of four sulfurs.
-S-S-

Another factor in support of branched chains is found in the reactions of the polythionic acids. The decomposition of the higher acids of this group results in the formation of the trithionic rather than the dithionic acid. The structures depicted in figure (1) are compatible with this view, as three sulfurs are linked together in a chain, whereas the additional sulfur atoms are linked by coordinate bonds which would be less stable than the bonds between the atoms in the chain.

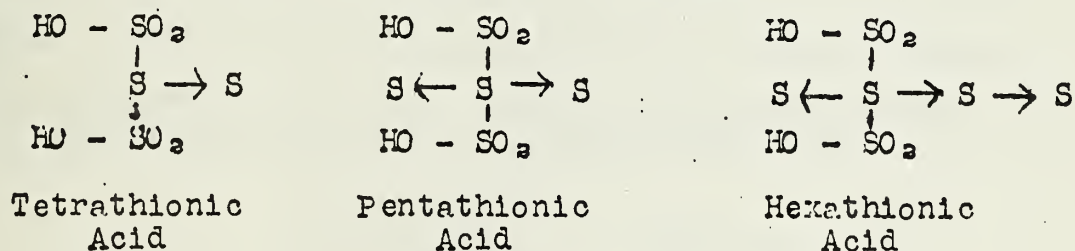


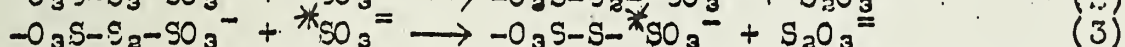
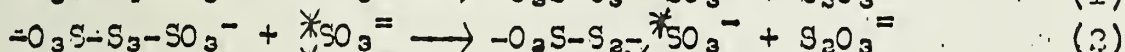
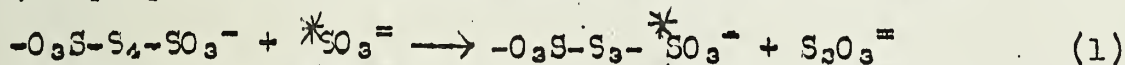
FIGURE 1

In view of recent data obtained by X-ray and electron diffraction methods; however the above structures do not represent the actual structure of these compounds. In fact, Foss (3) has questioned the ability of divalent sulfur to add sulfur atoms to its free electron pairs. He explains his point of view on the basis of the behavior of donor and acceptor atoms. Sulfoxides, R_2SO , selenoxides, R_2SeO , amine oxides, R_3NO , and phosphine oxides, R_3PO are stable substances, but such compounds as amine sulfides, R_3NS , and amine selenides, R_3NSE , have not been prepared. This suggests that stable compounds are formed only when the donor

atoms are less electronegative than the acceptor atoms. On this basis, the branched chain structures for the polysulfides and polythionates are feasible only if the sulfur in the chain becomes less electronegative than the branched sulfur atom. Whether or not this condition is fulfilled will depend upon the other groups attached to the donor sulfur atom. In dimethyl sulfide the sulfur atom should become less electronegative, so one might expect the formation of the structure, $(CH_3)_2S \rightarrow S$. However, there is no evidence for its existence. Therefore, compounds in which the sulfur is more electronegative than in dimethyl sulfide should be even less likely to exist as branched structures. The polysulfides and polythionates would fall in this class.

It has been suggested that branched structures might result from the formation of double bonds which would necessitate expanded valency shells for the divalent sulfur atoms. There are some indications that such configurations are possible in certain compounds, but these examples are uncommon and are unlikely to exist in the compounds under consideration.

If the above reasoning is correct, it does not seem likely that the polysulfur compounds exist as branched structures. Therefore it is desirable to explain the chemical behavior of these on the basis of linear chains. Various physical measurements have been interpreted to favor this configuration (4)(5)(6)(7), but the chemical properties did not seem as favorable. However, recent work with radioactive sulfur indicates that these properties may be explained in terms of the linear chain (3)(8). The reactions between polythionates and sulfite were studied and the following ionic displacement reactions proposed:



Foss suggests that the polysulfides react in a similar manner.

The behavior of elemental sulfur, which has been shown to consist of eight atoms arranged in a ring (Figure 2),

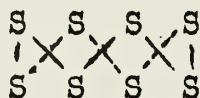
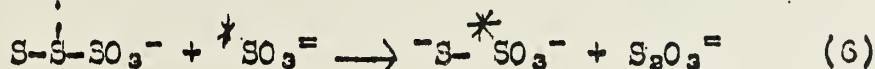
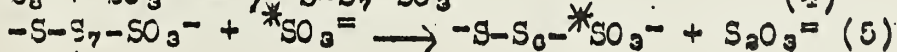
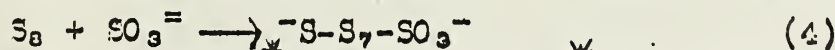


Figure 2

appears to agree with the above reactions. The first step in the reaction between sulfur and sulfite is the attachment of a sulfite to one end of the sulfur chain after the sulfur chain has undergone an "ionic opening". Then, successive ionic displacements of thiosulfate by sulfite take place. The proposed equations are:



The similarity between these and the above reactions with the polythionates lend support to the linear chain theory for the latter compounds.

Thus, on the basis of the evidence available at the present it appears that the linear chain configuration more likely accounts for the physical and chemical data on the polysulfide and polythionic compounds. Future investigations should clarify this problem more conclusively.

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SPECTROMETRIC STUDIES OF SOME COBALT (II) COMPLEXES.

Laurence F. Dempsey

April 3, 1951

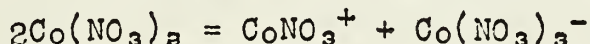
The color changes of some cobalt salts between a salmon-red and a pure blue have been known for many years. Some years ago two extremes of interpretation became differentiated. The one holds that the principal basis for the color change is a change in the hydration of the cobalt, the lower hydrate corresponding to the blue form. The second school holds that the effect is due to formation of a chemical complex such as CoCl_4^{--} . Various hybridizations of these extreme views have been proposed.

The data on the halide behavior have been extrapolated to the color changes of other cobalt salts so that the tendency has been to interpret all colors as gradations between the red and the blue forms, and hence often as semi-quantitative measures of the degree of admixture of the two forms. An assumption implicit in this procedure is that all tendencies toward visual bluishness represent the same structural alterations and presumably the same spectral changes. This implies further that a given intermediate color should be represented as a mixture of two spectra, that characteristic of the pure red form and that characteristic of the pure blue.

Studies were undertaken by Leonard I. Katzin and Elizabeth Gebert at the Argonne National Laboratory to show that these two interpretations are not independent.

Solutions of cobaltous nitrate in organic solvents show a magenta color, the shading of which is toward red rather than toward blue, and the intensity of which is a function both of the concentration and of the solvent. The absorption coefficient in each case falls off rapidly as small amounts of water are added to the solvent until the water content is ten per cent by volume, at which time differences become almost indistinguishable. Moreover, the addition of tetrabutylammonium nitrate to the original solutions increases the absorption coefficient. Presumably, therefore, these changes can be accounted for by complex formation, which is facilitated by lowering the dielectric constant, and which is reversed by the addition of water. To obtain a formula for this complex, the method of continuous variations was used. If two reagents which form an additive complex are mixed to a fixed concentration, the concentration of the complex is a maximum when the reagents are in the stoichiometric proportion in which they appear in the complex. Plotting a suitable property of the complex against concentration of the reagents should give a maximum at the ratio corresponding to the formula of the complex. When optical density in excess of that due to cobaltous nitrate was plotted against concentration, a maximum was obtained at a ratio of one mole of the $\text{Co}(\text{NO}_3)_2$ to one mole of NO_3^- both in acetone and in tertiary-butyl alcohol as solvents; thus a

complex of the type $\text{CoX}_3(\text{NO}_3)_3^-$ was indicated. If lithium nitrate was used instead of the tetrabutylammonium nitrate, the same result was obtained in acetone but not in t-butyl alcohol. The proof of the existence of the trinitrato complex does not give any evidence of undissociated cobaltous nitrate nor of the disproportionation of cobaltous nitrate according to the following:



To determine the extent of this disproportionation, nitrate ions were to be added to cobalt perchlorate by the method of continuous variations, but surprisingly enough, it was found that the perchlorate solution behaved analogously to that of the nitrate, although, as was to be expected, the perchlorate complex with cobalt seemed to be much weaker than that of the nitrate. To avoid interferences due to formation of such a perchlorate complex, measurements were made at a wavelength of 300 millimicrons, in which region the cobalt perchlorate was optically clear. Since, however, acetone absorbs in this region of the ultraviolet, further experiments were all carried out in t-butyl alcohol. Application of the continuous variations test with lithium nitrate and cobaltous perchlorate indicated a complex with two nitrate ions per cobalt ion, and the absorption coefficient of this complex was identical with that of pure cobaltous nitrate alone. If excess LiNO_3 were added, the absorption of the solution in the ultraviolet is just the sum of the absorptions of the two components, but if tetrabutylammonium nitrate were used instead, an excess density peak at the expected ratio of three nitrate ions per cobalt ion was obtained, but this excess density was very small. From these results it is concluded that the difference in the light absorption of dilute aqueous cobaltous salts and cobalt nitrate in organic solvents rests in formation of undissociated cobaltous nitrate in the organic media. In the presence of excess nitrate ions a fairly unstable trinitrato complex of cobalt does form.

To explain these results it is proposed that as increasing proportions of an organic base such as t-butyl alcohol are added to an aqueous solution of cobaltous nitrate, there will occur competition between water and the organic base for the solvation positions, and two molecules of water will be replaced first, then a third water, a fourth, and finally the last two waters will be lost as a pair. As the proportion of organic component in the solution increases, the dielectric constant drops, and the electrostatic attraction of oppositely charged ions increases. Eventually the anions in turn become electron donor competitors for the coordination positions around the metal atom. In this three-way competition for the coordination positions, the nitrate ion becomes a strong contender when the dielectric constant has dropped to about 20, as is shown by the strong association of cobaltous nitrate in acetone, which has a dielectric constant of 19.1. In an oxygenated anion like the nitrate, coordination to a cation produces a structural strain which accounts for the high absorption coefficient of cobaltous

nitrate in organic solvents; when small amounts of water are added the absorption coefficient drops very rapidly because water molecules are replacing the coordinated nitrate ions which now reassume their normal electronic grouping, and their normal spectrum. That these nitrate ions are no longer coordinated does not mean that the hexasolvate is 100% ionized, however, but rather that the ions are now attracted electrostatically to the positive ions.

Similar experiments were carried out with cobaltous chloride with similar results. The $\text{Co}(\text{H}_2\text{O})_6^{++}$ which exists in water solutions is pink, the undissociated CoX_4Cl_2 which exists in methanol is rose to magenta, and the CoX_2Cl_2 which exists in the higher alcohols is blue. By adding lithium chloride to solutions of cobaltous chloride in acetone and similar solvents complexes of the type CoXCl_3^- and CoCl_4^{--} can be formed, but of these two, the trichloro complex is the more stable. The addition of some complexing agent such as pyridine to an acetone solution of the tetrachloro complex will convert this readily to the trichloro complex, in which case one mole of pyridine has replaced one mole of chloride ions.

From these experiments it has been concluded that:

1. The so-called red form consists of hexacoordinated cobalt (II) ions.
2. The first complex to form, and the most stable when formed, is undissociated cobaltous nitrate or cobaltous chloride with four mols of solvent coordinated to the cobalt to maintain 6-coordination.
3. The color of the undissociated tetrasolvate is not red, but magenta; the blue tinge is not due to a complex of the type similar to the cobalt halides, but seems to be due to intensification of the normal cobalt absorption, and a broadening toward longer wave lengths. Blueness need not indicate complexes of the halide type, and absence of a blue color does not indicate absence of coordination.
4. The so-called blue color seems to be due to tetra-coordination as existing in the forms: CoX_2Cl_2 ; CoXCl_3^- ; and CoCl_4^{--} .

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EXPLOSIVES

Fred McCollough

April 10, 1951

HISTORY (2)

While gun powder has been known only since the 13th century, two of its constituents have been known from ancient times: sulfur and charcoal. The early history of gunpowder and explosives is closely connected with the discovery of methods of preparing and purifying the third ingredient: saltpeter. The discovery of gunpowder is usually credited to Roger Bacon although there is a legend of an earlier Chinese discovery. The gun powder was made by simply grinding the ingredients together in a mortar. At first, the powder was used in the fine state; but later it was discovered that "corning" the powder was advantageous.

The next step in the development of better explosives was the attempt to substitute $KClO_3$ for saltpeter. While this gave a more powerful explosive, the instability of the material made it unsafe to manufacture and handle. Gun cotton was discovered in 1845, and nitroglycerine in 1846. Alfred Nobel, in 1861, devised the first practical means of detonating nitroglycerine - the fulminate cap. This discovery, together with that that Kieselguhr had the power to absorb 3 times its weight of the explosive, lead to the development of dynamite. In 1871, Dr. Herman Sprengel patented his "Sprengel explosives" - mixtures of an oxidizing agent with a combustible one.

Since that time, there has been two great wars; and the development of explosives has been carried on at a great rate. While hundreds of materials function as explosives, the large scale industrial explosives are few in number. The important military explosives are: black powder, smokeless powder, TNT, amatol ($TNT + NH_4NO_3$), ammonium picrate, nitrostarch, etc.; and the important commercial explosives include black powder, dynamite, blasting gelatine, and NH_4NO_3 .

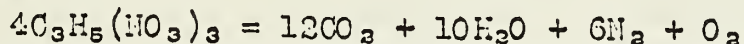
THEORY OF EXPLOSIVES (1,3,4,5,6)

An explosive can be looked upon as a chemical combination of atoms in a metastable state which spontaneously, on the passage of a detonating wave, rearrange themselves to give single products with the concurrent liberation of a large volume of gas and considerable energy. This energy, mainly in the form of heat, raises the temperature of the gas, thus greatly increasing its volume and contributing largely to the force of the explosion. If the velocity of the explosion is great, the explosion will produce a shattering effect. It is the shattering effect which earns the name brisant explosive.

There are six important characteristics towards which attention should be directed in a discussion of explosives:

1) The nature of the chemical change for the material in question, usually expressed as a chemical equation.

Most practical explosives produce the necessary physical phenomena as the result of a chemical change, and for them stoichiometrical relations can always be established to some degree. Thus nitroglycerine explodes:



Where organic explosives are concerned, it is customary in writing the probable reaction, to distribute O first to C to form CO, then to H to form H₂O, and finally to CO to form CO₂. Where other atomic species are also present in the molecule, the O or other oxidizing species is usually assigned to the combination which is most stable.

An explosive like TNT, which does not contain enough O to oxidize completely the final products, is said to have a negative oxygen balance. One like nitroglycerine, which has excess O, has a positive oxygen balance. The oxygen balance is given as the % of O required for complete conversion of the C and H to CO₂ and H₂O. For a compound containing x atoms of C, y atoms of H, and z atoms of oxygen, the oxygen balance is given by:

$$O.B. = \frac{y}{-1600(2x + 2 - z)} \text{ molec. wt.}$$

2) The heat of reaction for conventional weights of materials. Most explosive reactions are exothermic overall. The heat evolved may be measured experimentally or calculated theoretically. The result of explosion is the production of high explosion temperatures at which water (and sometimes other substances) is a gas. Explosive compounds may be either endothermic or exothermic.

3) The amount and type of energy required to initiate the reaction, that is, the sensitivity.

An explosive is a system which has the latent capacity to undergo a certain type of reaction which will not manifest itself unless the system is disturbed. The required disturbance is the application of energy in the form of heat, the mechanical energy of a blow, or by the detonation of another explosive near by.

4) The maximum temperature developed by the reaction.

5) The speed of the reaction, which may be expressed as the rate of burning of the material, or the velocity of propagation of explosion through the explosive. Given the possession of the other properties requisite for explosion, probably the most determining factor of total force is velocity of detonation. The difference between low speeds - less than 1000m/second - and high speeds is accompanied by a qualitative difference in effective power. This is the basis for classification into low and brisant explosives.

6) The power of an explosive - that is, its ability to do work - is measured in several ways, (e.g.) the Trautzel lead block test and the ballistic mortar. The former makes use of

the expansion caused in a pure lead block, while the latter measures the angle of recoil when a charge is fired in a heavy pendulum mortar. The latter value is uncomplicated by brisance.

The first effort to develop a relationship between performance and structural composition was made by Pletz (7) with his theory of "explosophores" and "auxoexplosives". While the arrangement of Pletz covers the whole field of explosives in a purely empirical fashion, the distinction between his terms is vague.

During the war, a complete survey of the field of explosives was made by Dr. A. H. Blatt. With this information, new studies have been made to try to correlate structure with explosive properties. If we plot power against oxygen balance, using this data, the result is a jumble of dots on the coordinates. However, if we introduce the concept of plosophoric groupings, this confusion is resolved. Here, we define a plosophore as a group of atoms, which on substitution into a molecule, is capable of forming an explosive compound. Plosophores are divided into primary and secondary groups, depending on the degree of effect they have on molecules containing them. The primary plosophores are: nitrate esters, aromatic and aliphatic nitro compounds, and nitramines. Secondary groups include: azo, azide, nitroso, peroxide, perchlorate. Plots of power, detonation velocity, sensitivity and heat of explosion against oxygen balance all give consistent curves for compounds containing primary plosophores. This shows a definite correlation between these properties and structures. These plots further show that these properties increase with increasing oxygen balance to a maximum at oxygen balance equal zero. Secondary plosophores do not show this clear-cut correlation. It is further shown that the effect of secondary groups on a molecule is less than that for primary. Also present in the molecule may be "auxoploses" which serve only to alter the explosive property. Examples are: $-OH$, $C=O$, $-Cl$, $S^=$, etc.

APPLICATIONS

Knowledge of the types of materials or mixtures which may be expected to decompose with explosive violence will help to avoid many accidents. Many molecules contain within themselves, potentially dangerous energy. This energy is derived mainly from the oxidation of C and H to CO_2 and H_2O and from the formation of molecular nitrogen. A compound containing any appreciable amount of O as well as N should be suspected. The presence of plosophores and auxoploses in a molecule also indicates potential explosive properties. One of the unusual cases which had escaped attention for many years is the group of oxygenated metal ammine complexes. Many of these compounds are prepared in laboratory courses. Some are powerful explosives. Recent literature contains many references to the explosive nature of these compounds. (8)

The recombination of atoms from a relatively weak bond state to a more stable state may also occur where two or more components are brought together in proper proportions, and where the energy of reaction is such that its release is rapid. Thus,

the association of an oxidant and reductant can be just as dangerous as a single explosive compound. (8)(12) Many inorganic mixtures contain oxidants and reductants, the general properties of which should be carefully considered before they are mixed. Following are some of the more hazardous mixtures:

- 1) Chlorates mixed with red P, S, C, and/or powdered metals
- 2) Chlorates mixed with acidic substances
- 3) Ammonium perchlorate, ammonium and inorganic picrates, ammonium nitrate used in inorganic mixtures (10)(11)
- 4) Peroxides mixed with P, S, C, etc.
- 5) Mixtures containing silver or lead salts
- 6) Mixtures containing permanganates and powdered metals, S, P, C
- 7) Many vapors form explosive mixtures with air (9) (3)

How may we avoid accidents in the laboratory? The first thing, of course, is to recognize the dangerous and unstable materials. Then, whenever such materials are being used, the following precautions might be suggested:

- 1) Since dangerous reactions generally require energy for their initiation, avoid anything that might furnish this energy such as open flames, electric energy (static or current), or the impact of two hard surfaces.
- 2) Conduct any operations involving vapors or gas in a hood.
- 3) Keep reagents stored so that there is no possibility of forming dangerous mixtures in case of breakage of the containers.
- 4) Unnecessary chemicals should not be allowed to accumulate in the laboratory.
- 5) Protective equipment must be utilized wherever applicable.

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GETTERS FOR HIGH-VACUUM ELECTRONIC TUBES

Hierle Winters

April 17, 1951

The expense involved in the removal of traces of gas in electronic tubes after evacuation of these tubes is more than compensated for by the increased life of the tubes. The gases are not actually removed from the tube, but are allowed to react with an active substance to form a solid compound which is, in effect, the same as removing the gas. The substances that are placed in the tube to react with these last traces of gases are called getters.

There are two distinct types of getters. One type is coated on the filament and carries on its work of combining with gases during the filament's operation at high temperatures. The other type is the "flash" getter. It is an active, fairly easily volatilized metal or alloy which is vaporized after the tube has been evacuated and sealed.

The residual gases that are to be removed by the getters are oxygen, nitrogen, carbon monoxide, carbon dioxide, and water vapor.

Coating Getters

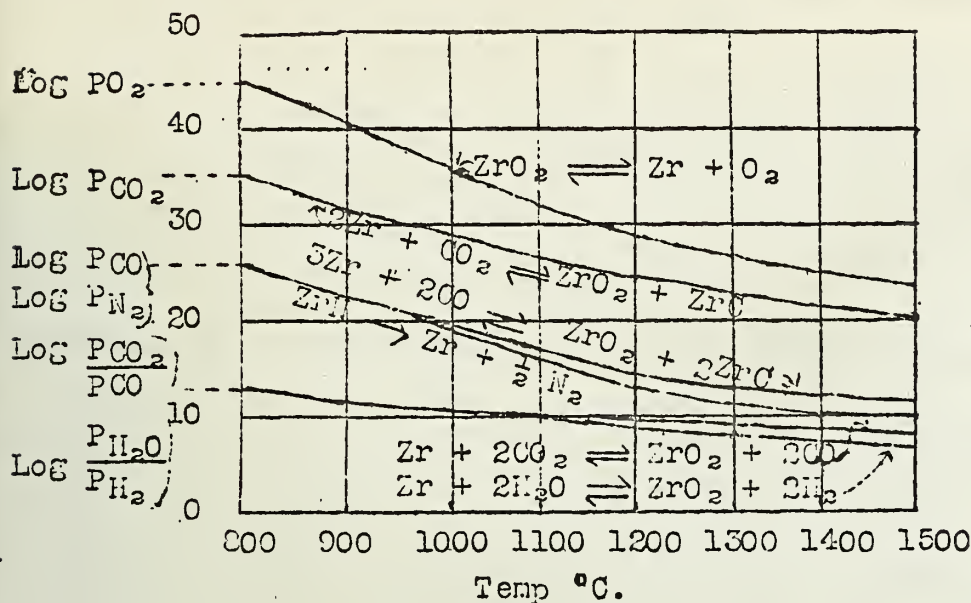
The most efficient metals currently being used as coating getters are tantalum, zirconium, thorium and a mixture of cerium and thorium.

In order to consider a metal for possible use as a coating getter, one must study the kinetics of the reaction of this metal with the gases mentioned above. A study of the reactions of zirconium will be described to illustrate the properties of a typical coating getter.

The following reactions are evaluated from calculation of free energy of formations in Figure 1:

1. $\text{Zr(s)} + \text{O}_2(\text{g}) \rightleftharpoons \text{ZrO}_2(\text{s})$
2. $2\text{Zr(s)} + \text{CO}_2(\text{g}) \rightleftharpoons \text{ZrO}_2(\text{s}) + 2\text{ZrC(s)}$
3. $3\text{Zr(s)} + 2\text{CO(g)} \rightleftharpoons \text{ZrO}_2(\text{s}) + 2\text{ZrC(s)}$
4. $\text{Zr(s)} + \frac{1}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{ZrH(s)}$
5. $\text{Zr(s)} + 2\text{CO}_2(\text{g}) \rightleftharpoons \text{ZrO}_2(\text{s}) + 2\text{CO(g)}$
6. $\text{Zr(s)} + 2\text{H}_2\text{O(g)} \rightleftharpoons \text{ZrO}_2(\text{s}) + 2\text{H}_2(\text{g})$

Fig. 1 - Equilibrium Calculations of Zr reactions



Evaluation of this graph tells us that ZrO_2 , ZrN , and ZrC are stable at all temperatures up to at least 1500°C and that zirconium can be expected to remove O_2 , H_2 , CO and CO_2 at the lowest pressures now being used in high-vacuum electronic tubes.

The reactions of zirconium with the individual gases

have been studied as a function of pressure, temperature, time and surface treatment.

The reaction of zirconium with oxygen is complicated by a protective oxide film formation, solution of the oxide at various temperatures, and transition from one form of the oxide to another at certain temperatures. In general, the reaction rate is considerable at first and gradually lessens; the film thickness is greatly increased with increasing temperature; an abraded surface is much more reactive than a non-abraded surface; and the effect of pressure is inversely proportional to the thickness of the oxide film.

Zirconium nitride formation as a function of time and temperature produces the same characteristic curve as the oxide formation. Evidence for the solution of the nitride film in the metal was obtained by allowing the nitride film to be formed and then removing the nitrogen atmosphere. A study of the surface of the solution (after standing) indicated that there was no longer a film on it and that the film previously observed had evidently dissolved in the metal.

With hydrogen, the reaction rate is proportional to the square root of the pressure at a given temperature. At a pressure of 22 mm. of Hg, zirconium begins to react with hydrogen at a temperature of 235°C . The upper limit of stability of the hydride was found to be approximately 436°C at a pressure corresponding to that used in high vacuum tubes (10^{-6} mm of Hg).

A typical method of coating a base metal with a getter will be illustrated with thorium which is currently a commercially important coating getter. The base metals (Fe, Ni, or Ag for examples) are prepared for the coating by reduction of any oxide films by means of a stream of hydrogen at a temperature of $800-1000^\circ\text{C}$. The pure thorium metal powder is usually obtained from Calcium reduction of

the oxide followed by purification to eliminate the excess calcium. This powder is made into a colloidal paste and either applied by brush or by cataphoretic deposition. The powder is simultaneously sintered to the base and degassed in a vacuum furnace at a temperature dependent upon the base metal used.

Certain alloys have also been found to possess the characteristics of good getters. A good example of these is the Ceto alloy. The name is a contraction of Cerium and Thorium. Its best feature is its marked getter action at temperatures considerably lower than must be used with other getters. Special care must be exercised in sintering this material to prevent the reduction of its getter activities at the casting temperature.

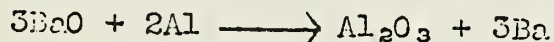
Advantages and disadvantages of the two Getter Types.

The flash getter does not require as much preliminary processing as the coating getter and is, therefore, the more inexpensive of the two. But undesirable spattering may result when the flash getter is volatilized. This may be reduced by the use of specially constructed mounts for the getters and by shielding the parts that should be protected. The mirror formed by the condensation of the getter vapors on the inside wall of the tube inhibits the cooling of the filament by radiation and, in short wave tubes, may produce capacity effects. It is also possible for the vapors to condense on other cool parts of the tube; this may result in the formation of a conducting layer over an insulator. Coating getters are usually used in tubes in which the high temperature required for the "flashing" is undesirable.

Flash Getters

The active ingredient of most flash getters is barium, either alone or in combination with aluminum, calcium, strontium, or magnesium. The getter is made into the form of a pellet and is placed in the tube on a special mount. After the tube is evacuated and sealed the getter is flashed (volatilized) by electron bombardment or high-frequency heating.

Getters of pure barium react readily with oxygen and water vapor at room temperature during the insertion operation to form BaO and $Ba(OH)_2$. This reduces the effectiveness of the getters. For this reason, a mixture of the oxide of barium and aluminum is used to start with. After insertion in the tube, the pellet is heated to a sufficiently high temperature to set off the thermite reaction.



in which the vaporized Barium is released to perform its getter duties.

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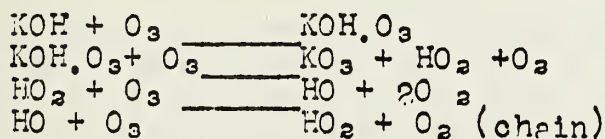
"OZONATES" OF THE ALKALI METALS

Dale E. Woerner

April 24, 1951

Curiosity concerning the products of the action of ozone upon the alkali metal hydroxides has been evident since the first mention of this reaction by Wurtz (4) in 1868. Various formulae were assigned to these products, among them M_2O_4 , MHO_4 , $M_2O_7 + M_2O_4$, $(MOH)_2O_2$, and $MOH.O_2$; none of these has completely satisfied workers in this field. It now appears that the formula MO_3 , first proposed by Kazarnovskii, Nikolskii, and Abletsova (1) in 1949, and later confirmed in part by Whaley (2), best describes these products. At one time these salts were considered derivatives of the hypothetical ozonic acid ($H_2O + O_3 \rightarrow H_2O_4$) and were thus called "ozonates".

Potassium ozonate was prepared by passing ozone-containing oxygen (6 to 8% ozone) through desiccated, finely pulverized KOH at $-15^\circ C$. After several hours of the ozone treatment, the system was flushed with dry oxygen. A trace of water is necessary in both the ozone and the hydroxide for the reaction to proceed with an appreciable velocity. CsOH and NaOH were ozonated in the same manner. The formulation is thought by Kazarnovskii et. al. to proceed in two steps.



The orange colored product, KO_3 , is formed on the surface of the KOH particles and can be shaken loose therefrom. It is soluble in liquid ammonia giving a solution of red color; this affords a method of isolating this product. Orange-red CsO_3 is also soluble in liquid ammonia but the NaO_3 is not. The common organic solvents apparently effect no dissolution.

A solution of KO_3 in liquid ammonia has a molar electrical conductance at $50^\circ C$ of 34 ohm^{-1} . From this fact one may deduce the formula to be $K O_3$. The O_3 ion is thought by Kazarnovskii, Nikolskii, and Abletsova to be a resonance form either between $\bar{O}-O-\bar{O}$ and $-O-O-\bar{O}$ or among $\bar{O}-O-\bar{O}$, $O-\bar{O}-\bar{O}$ and $\bar{O}-\bar{O}-O$. X-ray work done by these workers point toward a similarity between the lattices of KO_3 and KN_3 , the latter anion being of a linear configuration.

Measurements of magnetic susceptibility gave results which led to the establishment of the magnetic moment as being 1.67 (1) or 1.63 (2). Bohr magnetons for

for the paramagnetic potassium ozonate. Since these values correspond quite well to the theoretical value for one unpaired electron (i.e., 1.73 Bohr magnetons), the formulas K_2O_3 and $\text{KOH}\cdot\text{O}_3$ are ruled out.

Stabilities of these compounds are highly dependent upon both the temperature of preparation and the temperature of decomposition. The ozonated sodium hydroxide proved to be stable at room temperatures for over 18 months (2). Above 100°C it decomposes to give O_2 and NaOH . The potassium product is decolorized in several hours at room temperature while CsO_3 is only partially decomposed after several days (2). At 50° to 60°C , decomposition of KO_3 is complete in 30 minutes. Liquid ammonia extracts of CsO_3 and KO_3 decompose violently in the presence of water, producing flashes of light and evolving oxygen.

Ozonated KOH and CsOH react with acidified solutions of KI to liberate iodine. The higher the temperature of formation, the less iodine do they produce. Ozonated NaOH gives no reaction with acidified KI solution even after 18 months standing. In water or acid, all three ozonates liberate oxygen. Negative peroxide tests are obtained with fresh and aged ozonated hydroxides of the three metals.

The liquid ammonia extracts of cesium and potassium ozonates react with acidified KI solution to give iodine but again no peroxide tests are obtained. In their reaction with water, oxygen is liberated and the resulting solution is capable of oxidizing HI solution. Upon being heated for approximately one hour, both extracts change in color from red to a mixture of yellow and white. The yellow portion responds to a peroxide test, indicating formation of either H_2O_2 or MO_2 .

W haley (2) uses magnetic data to support his contention that his products are principally MO_3 . Magnetic and chemical analysis of the ozonated NaOH show NaO_3 to be a quite satisfactory formulation for this compound. He states that the potassium and cesium products may well be mixtures, since NaO_3 does not oxidize iodine ion. Upon analysis of the products resulting from the complete decomposition of KO_3 , the latter was found to have contained 55% K_2O , and 45% available O_2 (theoretical for KO_3 : 54.1% K_2O , 45.9% O_2) (2). Kazarnovskii et.al. reported decomposition of the liquid ammonia extract of the potassium compound as follows: before, 93.4% KO_3 , 5% KOH ; after, 39.8% KO_2 , 8.6% KOH (1).

Ozonation of concentrated alkali solutions and of

sodium and barium peroxides was undertaken by Whaley (3), and an increase in paramagnetic character was noted in most cases.

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THE DIRECTIVE INFLUENCE OF THE NITRO GROUP IN THE NITRO COMPLEXES OF PALLADIUM (II)

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The existence of the cis series of Pd(II) amines has been questioned by many authors. (1) The pink crystals of cis-dichloro-ammine palladium(II) were claimed to be crystals of a dimer rather than the cis isomer. This dimer was supposedly $\text{Pd}(\text{NH}_3)_4\text{Pd}(\text{NO}_2)_4$. The cis-isomer was prepared by Mann. (2) The cis compound differed from the trans compound in all its properties. X-ray investigation showed the cis complex to have eight molecules per unit cell as compared to one for the trans compound. A large number of molecules per unit cell is usually found for the unsymmetrical cis compounds. (3,4,5)

The cis-dinitrodiammine palladium(II) isomer is unusual in that its preparation seemingly is a complete reversal of Tschernaiev's (Chernyaev's) rule of trans-elimination. (6) The rule of trans-elimination indicates that groups having a large trans-influence cause the group in the trans position to have an increased tendency for displacement. Trans-influence is inversely proportional to the metallic character of the group. (e.g. the more electronegative group such as the nitro group has a higher trans-influence than the Cl^- and so forth). According to this rule Nitrite ions added to a solution of tetra-ammine palladium(II) ions should result in the formation of the trans-dinitrodiammine compound rather than the cis compound. (2) Similarly the addition of ammonia to a solution of tetra-nitro palladium(II) ions should form the cis compound rather than the trans isomer which is always obtained. (2) The present work proposes reaction mechanisms which account for these "exceptions" to the rule of trans elimination.

Three tests were found applicable to distinguish between the cis and the trans dinitrodiammine complexes. (2) (7)

- (1) cis isomer plus KI gives colorless solution;
trans isomer plus KI gives a red colored solution;
- (2) cis isomer melts at $233-234^\circ$, no evolution of gas;
trans isomer melts at $230-231^\circ$, with evolution of gas;
- (3) Ignition; cis isomer decomposes quietly leaving black or grey compact residue.
trans isomer, exothermic decomposition,
heat and light given off, grey porous residue.

A study of the reactions between dichlorodiammine palladium (II), ammonia and sodium nitrite in aqueous solution was carried out. (7) The procedure consisted of measuring the initial pH and the pH as each crop of crystals was removed. The crystals were allowed to form as the mother liquor stood in a desiccator over conc. sulfuric acid. The decrease of pH with increased time was due to absorption of ammonia by the acid. The crystals were placed in labeled weighing bottles and tests were made to determine whether they were the cis or trans isomers. A compilation of all results obtained are given in table I.

TABLE I

Study of $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ formation from $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. (6)

Soln. no.	Total % cis	Total % trans	Total % yield	Time reacn., hr.	pH at transi- tion	Remarks
1-A	52.3	27.2	79.5	48	9.33	Mann's cond.
2-A	40.9	31.9	72.8	104	9.52	" "
3-A	52.5	23.0	75.5	114	9.70	" "
1-B	52.5	23.0	75.5	114	9.70	Mann's Cond. (8:1)
2-B	50.0	20.6	70.6	114	9.65	$(\text{NO}_2)_2\text{Pd}(\text{II})$ (6:1)
3-B	36.4	13.7	50.1	96	9.48	" " (4:1)
4-B	50.3	6.9	57.2	115	9.42	" " (2:1)
5-B	40.9	27.6	68.5	96	9.80	" " (10:1)
6-B	43.4	27.3	70.7	96	9.87	" " (12:1)
1-C	45.5	20.6	66.1	96	9.94	$\text{NH}_3:\text{Pd}(\text{II})$ (3.2:1)
2-C	59.2	20.6	79.8	96	9.98	" " (6.4:1)
3-C	52.5	23.0	75.5	114	9.70	Mann's Cond. (8:1)
4-C	43.2	23.0	66.2	96	9.96	$(\text{NH}_3):\text{Pd}$ (10.2:1)
1-D	52.5	23.0	75.5	114	9.70	Mann's Cond. 0.38M
2-D	4.6	50.2	54.8	129	9.94	$\text{Pd}(\text{II})$ 0.24M
3-D	-0-	73.2	73.2	156	" 0.16M
4-D	-0-	75.4	75.4	228	" 0.12M
1-E	-0-	77.6	77.6	42	Temp. 35-40°
2-E	-0-	61.7	61.7	42	" "
3-E	59.1	38.8	97.9	256	10.99	" 10-13
4-E	68.2	27.5	95.7	192	10.89	" "
1-F	45.7	34.2	79.9	84	7.75	Sub. of NH_4NO_2
2-F	43.4	45.5	88.9	84	7.79	(for NaNO_2
1-G	-0-	82.0	82.0	178	Sub. Cis + trans
2-G	-0-	77.4	77.4	178	$\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$
3-G	-0-	63.8	63.8	68	as starting
4-G	-0-	77.4	77.4	68	material at 25°
5-G	-0-	59.4	59.4	160	at 10°
6-G	-0-	69.0	69.0	160	at 10°
1-H	61.5	9.0	70.5	239	9.88	Addn. of Cl^- at 10°
2-H	52.4	9.0	61.4	239	9.77	" " " "
1-J	45.6	32.0	77.6	96	9.95	cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$
2-J	40.9	29.7	70.6	96	10.01	trans- " "

A- Mann's condition: 0.38 mole PdCl_2 in 3 moles of conc. NH_3 .
Heat, filter, then add 3 moles of NO_2^- ions.

B- Variation in NO_2^- ion concentration.

C- Variation in NH_3 concentration

D- Effect of Dilution.

E- Variation of Temperature.

F- Sub. of Ammonium Nitrite for Sodium Nitrite.

- G- Sub. of cis or trans dinitrodiammine complex for dichlorodiammine.
- H- Use of dinitrodiammine complex as starting material and then adding two equivalents of NaCl.
- J- Use of either cis or trans dichlorodiammine complex.
- - - - -

The reactions proposed to account for the results obtained were:

- (I) The reaction between dichlorodiammine complex and ammonia to give the chlorotriammine complex ion or the tetra-ammine complex ion depending on the ammonia concentration.
- (II) The reaction between the chlorotriammine complex ion with the nitrite ion to give the chloronitrodiammine complex ion which reacts further with the excess nitrite ion to give the cis-chlorodinitroammine complex ion.
- (III) The reaction between cis-chlorodinitroammine complex ion with ammonia to give the cis-dinitrodiammine complex.
- (IV) The reaction between cis-dinitrodiammine complex and ammonia and nitrite ion to give trans-dinitrodiammine.

A mechanism study was also made of the reaction between $\text{K}_2\text{Pd}(\text{NO}_2)_4$ and ammonia. In this case the cis-dinitrodiammine complex was only obtained at lower temperatures where its solubility was appreciably decreased. It was concluded under these conditions the chloride ion is not necessary for the formation of the cis isomer.

The reaction mechanisms which were postulated can explain the observed phenomena only if the rule of trans elimination is assumed.

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Introduction

Intense ultrasonic waves produce unusual physical, chemical, and biological effects. Pioneer work in chemical ultrasonics was done by Richards and Loomis in 1927 on the dispersion of colloids and the effect of ultrasonic waves on the rate of various reactions. (1). Since that time, many reactions involving ultrasonic waves have been discovered and investigated. There is general agreement among the investigators on the difficulty of getting quantitatively reproducible results, but not on many of the experimental facts and interpretations.

APPARATUS

The principle of an ultrasonic wave generator is simple. The apparatus ordinarily used consists of a power source which provides electrical energy at frequencies of from 300 to 2000 kilocycles. The electrical energy is fed to a quartz crystal transducer which is immersed in transformer oil. The reaction vessel is clamped a few centimeters directly above the crystal source of ultrasound. The Ultrasonicator, a commercially available apparatus, will provide up to 600 watts of electrical energy at several frequencies.

PHYSICAL BACKGROUND

The energy in an ultrasonic wave is carried through the medium by the back and forth motion of the molecules, which produces alternate compressions and rarefactions. In the specific case of a one megacycle wave of 10 watts / sq. cm. intensity in water, it can be calculated that the displacement amplitude is very small, less than 10^{-5} cm. However, the acceleration attains very high values, about 250,000 times greater than the acceleration due to gravity. The maximum instantaneous velocity of the particles is about 40 cm / sec.

In addition, there are considerable alternations of pressure between compression and tension at a given point in the liquid. In the case above, the pressure would be about 10^5 atmospheres. One effect of such great changes in pressure is cavitation, which is the formation and violent collapse of small bubbles or voids in the liquid. In the case of water saturated with air, the negative pressure portion of the sound wave causes some of the air to come out of the solution as minute bubbles, which act as weak spots for the further tearing-apart of the liquid to form larger cavities. Then, when the pressure increases, as in the other half of the sound wave cycle, the cavities collapse with a violent hammering action which generates local pressure up to thousands of atmospheres and local temperatures up to several hundred degrees. But if the water is freed from dissolved gases and suspended particles, its apparent cohesive strength is much greater and no cavitation occurs unless negative pressures of the 100 atmospheres are applied.

Among the first reactions observed caused by ultrasonic waves were the discharging of metastable states. Nitrogen triiodide can be exploded, and yellow mercuric iodide can be converted to the red modification below 120°. (1). Many other reactions have been observed, some of them partly understood, and others difficult to explain. Some of the reactions which have been observed are:

1. Liberation of I_2 from a KI solution. (2)
2. Production of H_2O_2 , NO_2^- and NO_3^- in water solutions containing air. (3)
3. Reduction of $KMnO_4$ solution. (4)
4. The rearrangement of benzazide. (5)
5. The selective degradation of certain amino acids in aqueous solution. (6)
6. Depolymerization of certain polymers. (7,8)
7. The rupture of lignin to cellulose bonds in wood pulp. (9)

The reaction which has received the most attention recently is the production of iodine when ultrasound travels through potassium iodide solution containing dissolved air. (2) Lin and Wu (10) stated that both oxygen and cavitation are essential, and found that adding a little carbon tetrachloride to the potassium iodide solution greatly increased the amount of iodine liberated.

In order to explain this reaction, Weissler, Cooper, and Snyder (2) undertook a quantitative, detailed study of the reaction, both in the presence and absence of carbon tetrachloride.

If, in the absence of carbon tetrachloride, the oxidation of potassium iodide is brought about by ultrasonically-produced hydrogen peroxide or nitrous acid, then equivalent quantities of free iodine and hydroxyl ion should be formed, according to such an equation as:



This was verified experimentally by titration with sodium thiosulfate and hydrochloric acid. The rate of iodine liberation in the absence of carbon tetrachloride is about one fifteenth of that when carbon tetrachloride is present.

Because of the poor reproducibility reported by earlier investigators, their first efforts consisted of evaluating the effects of certain experimental variables. After reaction vessels made of metal, polythene, porcelain, and glass had been tried, ordinary glass test tubes were selected as being most suitable from the standpoint of chemical inertness, availability, and magnitude of yield obtained. Different size test tubes gave widely varying results with no apparent correlation between yield and size or shape of the vessel. However, the yield did appear to be a periodic function of wall thickness. Presumably, more energy is passed through the wall of the tube when the wall thickness is an integral number of half-wave lengths. Positioning of the test tube was also found to be important.

Small vertical displacements caused large changes in the energy transmitted, because of the effect on the standing wave pattern in the oil. By careful control of experimental conditions, it was possible for these workers to attain a reproducibility of 5-10%.

Richards and Loomis (1) suggested that the chemical effects of ultrasonic irradiation are due only to the concomitant heating effect. However, Weissler and co-workers (2) argued that this seems unlikely in view of the small temperature coefficient observed by them when making runs on solutions at various temperatures. Generalized heating may not be responsible for the chemical effect, but the possibility still remains that the causative factor is the local temperature of several hundred degrees produced at the collapse of cavitation bubbles.

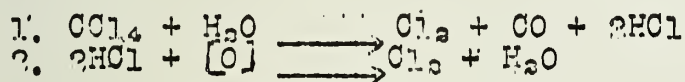
Weissler and co-workers determined that the concentration of potassium iodide has no effect on the rate of the reactions. This shows that the potassium iodide merely indicates the extent of another, more fundamental reaction which produces oxidizing agents. When carbon tetrachloride was used, the amount of tetrachloride had a greater significance. The yield of iodine increased with the amount of carbon tetrachloride up to a maximum, then it fell off as a second phase was formed. This was probably due to excessive scattering of the ultrasonic energy by the new phase.

Increasing the frequency from 400-1500 kc. while keeping the power input level constant caused an irregular variation in iodine yield. This is in agreement with other ultrasonically produced reactions (3, 4, 7). By changing the volume and power input, it was determined that there was an optimum energy density. This energy density seems to be the same for all frequencies. The larger the volume, the greater the power required to produce cavitation and free iodine.

Other types of cavitation than that produced by ultrasonic waves can be produced in a liquid. Weissler (2) discovered that no oxidation of potassium iodide was produced after ten minutes of vigorous cavitation in a Waring Blender. However Polotskii (3) was able to demonstrate the production of H_2O_2 , NO_3^- , and NO_2^- by nonsupersonic cavitation artificially produced by the introduction of superheated steam into a water solution saturated with air. This indicated that direct activation by supersonic waves of oxygen and nitrogen dissolved in water as suggested by most earlier investigators does not occur, but the activation is due to cavitation. Earlier investigators have also stated that dissolved oxygen is essential for the reactions. Weissler (2) carried out some experiments to confirm this. When Potassium iodide solutions were degassed by boiling under vacuum, no iodine was liberated with or without carbon tetrachloride. If the degassed solution is saturated with either pure oxygen or pure nitrogen, the yields are about the same as for air. (It has been shown that the oxidant nitrous acid is produced in solutions

containing nitrogen and hydrogen peroxide is produced in solutions containing oxygen. (5) Helium saturated solutions produced no iodine at all in the absence of carbon tetrachloride, but when carbon tetrachloride was added, almost as much iodine was produced as in the case of the air saturated solution. (2) This demonstrates that free chlorine is not liberated from carbon tetrachloride by activated oxygen or similar oxidant, as was stated by previous investigators. Instead, the carbon tetrachloride itself participates in the primary sonochemical reaction: the carbon-to-chlorine bond is broken by the large mechanical or electrical forces generated at the collapse of cavitation bubbles. With carbon dioxide, no iodine was produced in the presence or absence of carbon tetrachloride, even though cavitation occurs.

By further study of the KI-CCl₄ reaction, Weissler (2) was able to demonstrate that four atoms of oxidizing chlorine were evolved for every atom of carbon tetrachloride. To comply with their data, they suggested that two consecutive first-order reactions were taking place, the first more rapidly than the second, each producing two oxidizing chlorines per molecule. For the chemical nature of these reactions, the tentative proposal was made:



There is some evidence in favor of this scheme. The second reaction will occur when Hydrogen chloride solution is subjected to ultrasonic radiations and can be prevented by excess alkali. Also, the first reaction, which is practically complete in 10 min., produces hydrogen chloride; the second destroys it. This implies that the acidity will be maximum at ten minutes. This was confirmed experimentally. However, infrared and mass spectrometer analysis showed that carbon dioxide and not carbon monoxide was produced by irradiation of a mixture of water and excess carbon tetrachloride in a closed system from which all air has been replaced by helium. The carbon dioxide might arise from hydrolysis of some of the intermediate product phosgene, or from an ultrasonic reaction between carbon monoxide and water.

Many of the sonochemical reactions can be explained by the activation of dissolved gases or carbon tetrachloride to produce H₂O₂, NO₂⁻, NO₃⁻, or Cl₂. This activation is due to the electrical discharges or the tremendous heat, pressure, or mechanical effects produced when cavitation bubbles collapse. Such materials as potassium permanganate and potassium iodide merely serve as indications of such reactions.

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THE PRODUCTION AND USE OF SYNTHETIC GEMS

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Before the war synthetic gems were made in Monthey and Locarno Switzerland, Bitterfeld and Zwickau in Germany and Annency and Garrie in France. The daily capacity was between 750,000 and 1,000,000 carats, nearly 200 kilograms. The British decided to start production in view of the world situation in 1939. They sent scientists to Switzerland to study the process and provide a nucleus for a synthetic gem industry in England. (3)

The production of Sapphire and its large scale production into industrial parts was a wartime development in this country. The Elgin plant was the largest to enter this field and Linde Air Products Company was the first and largest commercial American producer of sapphire as a raw material. (5)

The artificial stones are the absolute equivalent of the real gems being neither forgeries or substitutes, for they possess basically the same chemical structure as natural stones. (2) Sapphire is harder and purer than emery, abrasive alumina and is harder than tungsten carbide. It is not, however, as hard as boron carbide, but tougher. Synthetic sapphire has a combination of hardness and toughness superior to that of any other man made material.

All ruby and sapphire whether genuine or synthetic is composed of aluminum oxide, the hexagonal form of alpha corundum. Minute traces of impurities such as titanium, iron, vanadium, and chromium are mixed with the 100% pure alumina powder, for it is only these metals that give the gem its characteristic color and brilliance. By adding 2 1/2% chromium oxide to alumina a red ruby is obtained, while if vanadium oxide is added the result is an alexandrite, a stone having a green fire by day and a red fire by artificial light. Blue sapphire is produced by a fraction of 1% titanium oxide or cobalt oxide. (8).

The sapphire is formed by feeding the aluminum oxide into an oxy-hydrogen flame and the fused material is deposited on a fire clay pedestal in a carrot shaped mass known as a "boule". Boules up to 750 carats and larger have been produced although in production 300 carats is the usual size. A carat weights 0.2 grams and the price per carat of white sapphire is about three cents.

After removal of the boule, a sharp blow on the stem will usually cause it to split in roughly symmetrical halves, the flat surfaces of which are essentially plane. X-ray examination shows that the boule is a single crystal and that the plane of splitting is not even on a principal crystallographic plane. It is generally believed that splitting the boule relieves internal stresses formed during the growing of the boule.

Three important physical characteristics feature synthetic ruby and sapphire. The first and most conspicuous is the formation of curved lines seen in the microstructure. These lines are created during the formation of the boule. The second characteristic of synthetic sapphire is the formation of gas bubbles. The bubbles are quite small and invariably round. They occur singly or in clouds, the latter consisting of hundreds of minute specks requiring magnification to discern. Lastly synthetic corundum on cooling invariably crystallizes in a state of strain. Attempts to eliminate strain by hours of annealing at elevated temperatures proved futile. Observations with polarized light will disclose the strain.

The chief distinctive features of genuine rubies and sapphires fall into two categories inclusions and crystallographic structure. The former may appear as rutile needles, canals, iron stains, irregularly shaped gas bubbles and liquid inclusion.

The specific and physical properties of both genuine and synthetic sapphire are for all purposes identical; therefore it takes a combination of many specialized techniques to differentiate conclusively.

	<u>Genuine</u>	<u>Synthetic</u>
Chemical form	Al_2O_3	Al_2O_3
specific gravity	3.99	3.99
Hardness, moles	9	9
Melting point	2030° C	2030° C
Crystal System	Hexagonal	Hexagonal
Indices	1.759 1.768	1.76 1.769

Elgin has developed applications of sapphire for burnish cutting tools, dimensional control gauges, ring gauges, thread guides in the rayon industry and in the ultra violet treatment of blood plasma and serums. It has also been used in scintillation counters, viscometers, for lenses and prisms and as valve seats and stems. Its uses in the past have been principally in the machine tool industry but more and more applications will be developed for the chemical industry (6)(7)(10)(4)(1).

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GEOCHEMISTRY AND THE CYCLE OF THE ALKALI METALS

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Introduction

As the name implies; geochemistry represents the border field between geology and chemistry. Various workers in the field have proposed more or less involved definitions of the scope and field of geochemistry. V. M. Goldschmidt, one of the foremost workers in this field, outlined what he considered to be the three main tasks of geochemistry and in so doing arrived at a most satisfactory definition (7):

- (1) Establish the abundance ratio of elements in the Earth.
- (2) Account for the distribution of elements in the Earth.
- (3) Detect laws governing the abundance relationships and the distribution of the elements.

Recognition of the three general rock classes is necessary in order to begin a discussion of the occurrence of elements in the lithosphere (the outermost crust of the Earth): igneous rocks result from the crystallization of molten magmas which have welled-up from the Earth's interior (e.g. feldspars, granite); sedimentary rocks result from the decomposition of igneous rock (or metamorphic rock) through weathering processes and the subsequent aggregating of these weathered products by increasing pressure and temperature (e.g. limestone); metamorphic rocks result from physical and chemical adjustments made by rocks below the weathering zone in order to meet the requirements of changing temperatures and pressures (e.g. marble)

A knowledge of general chemical properties will not always suffice to account for the occurrence and distribution of elements. This is due largely to the fact that the distribution of elements as a result of magma crystallization is governed to a great extent by the crystal structure of minerals and the size relationships which determine the ions capable of fitting into these structures. On the other hand the weathering process which results in a further distribution and separation of the elements involves both size and charge relationships, most frequently expressed as ionic potential (ionic charge: ionic radius) (4)

The crystallization of magmas to form igneous rocks might be considered as an example of large scale, incomplete fractional crystallization. The manner of deposition of elements during this period of magma crystallization is best understood by recourse to crystal chemistry.

The space requirements of a particle depend upon the equilibrium between the attractive and repulsive forces of the particle and its neighbors. Therefore, the "effective size" of an atom or ion in a structure will depend upon a number of factors: the nature of the binding forces, the electronic structure of the atom or ion, the polarizability of the particle, the number of neighboring particles (coordination).

In general the coordination of a cation in an essentially ionic structure depends mainly upon the cation: anion radius ratio.

<u>Coordination number of cation</u>	<u>Arrangement of anions around cation</u>	<u>Radius ratio cation: anion</u>
2	opposite one another	Up to 0.15
3	corners of equilateral triangle	0.15 - 0.22
4	corners of tetrahedron	0.22 - 0.41
6	corners of octahedron	0.41 - 0.73
8	corners of a cube	> 0.73

Since oxygen constitutes 92% by volume of igneous rocks, the radius ratio of cation: oxygen ion is of special importance from the geochemical point of view. Crystalline oxygen containing minerals may be considered as aggregates of large oxygen ions, the interstices being filled by cations. (12).

In the crystallization of magma by far the greatest number of minerals formed are silicates, the more abundant elements generally will form independent silicate minerals, while less abundant elements usually will be incorporated as trace constituents in those primary minerals whose structure and coordination are compatible with the size requirements of the less abundant element. The position replacement of one atom by another in a mineral structure has been designated as "diadochy" by various geochemists (9,10). This concept has proved useful in understanding the incidence of rare elements. The occurrence of trace elements is influenced by the size of the atoms or ions, the type of crystalline structure involved and the temperature conditions under which the mineral formed.

Diadochic substitution may occur for ions of unlike charge in which case electrostatic neutrality is maintained either by the simultaneous substitution of another ion, or by the introduction of an additional ion outside the regular structural framework, or by a defect-type lattice in which certain structural positions are vacant. Goldschmidt (6) distinguished three types of diadochy in the occurrence of trace elements:

- 1) Camouflage - trace element replaces common element of similar valence.
- 2) Capturing - trace element replaces common element of lower valence. Because of its higher charge, the trace element is incorporated into the structure more firmly than the common element.
- 3) Admission - trace element replaces a common element with a higher valence. This type of replacement weakens the structure.

Gibson (4) states that if the capture or demission of the trace constituent is less than 5%, electroneutrality may be maintained by a defect-lattice arrangement. However, if capture or admission exceeds 5%, the change in cationic charge is usually balanced by a change in anionic charge.

Since elements of the same ionic charge and similar size do not always exhibit diadochy, Goldschmidt attempted to show that

diadochy between such elements is influenced by the similarity of their ionization potentials. Tending to support this view are the following ionic pairs which are known to exhibit extensive diadochy: $\text{Si(IV)} - \text{Ge(IV)} = 1\%$ difference in ionization potential; $\text{K(I)} - \text{Rb(I)} = 4\%$; $\text{Zn(II)} - \text{Co(II)} = 7\%$; $\text{Mg(II)} - \text{Zn(II)} = 8\%$; $\text{Al(III)} - \text{Ga(III)} = 8\%$. In addition Goldschmidt's rule would predict that the pair $\text{Ag(I)} - \text{Cu(I)} = 50\%$ would exhibit no tendency towards diadochy, a situation which is found to be true in the case of ionic minerals. However, a number of cases may be cited which violate this rule: $\text{Rb(I)} - \text{Tl(I)} = 32\%$ difference in ionization potential, but these elements occur together in rocks; $\text{Fe(II)} - \text{Ni(II)} = 13\%$ and $\text{Mg(II)} - \text{Ni(II)} = 22\%$, yet nickel exhibits more geochemical relationships to Mg(II) than to Zn(II) (9).

The formation of igneous rocks by magma crystallization is usually considered as a three stage process (4): 1) the first crystallization, taking place above 1200° ; 2) the main crystallization occurring between $500-1200^\circ$; 3) the final crystallization, taking place below 500° . In both the first and main crystallization the principle solvent is silica while the primary cation solutes are iron, magnesium aluminum, sodium, and potassium. A small amount, probably not over 1%, of supercritical gases such as CO_2 , SO_2 , H_2S and H_2O is also present. These volatile constituents, although present, only to a slight extent, exert a relatively large effect on the viscosity and the temperature range of crystallization of the magma.

In the first stage of crystallization the magma wells up from the interior of the Earth to fill a reservoir two or three miles below the surface of the Earth. The higher melting constituents crystallize out and sink down through the molten magma bringing about differentiation. Further differentiation may occur in the movement of the magma through the surrounding rock in a sort of "filter press" operation.

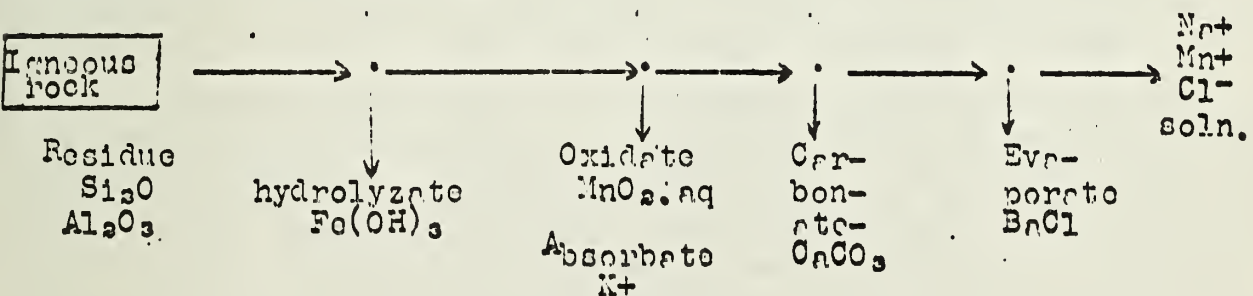
The main crystallization results in the formation of ortho-, meta-, and aluminosilicates with iron, magnesium, calcium, sodium, and potassium the predominate cations. The conditions for the main crystallization may occur in two different ways: the magma may be injected into fissures and cracks near the Earth's surface forming intrusive rock such as granite, or the magma may be ejected at the surface forming extrusive rock such as basalt. The first minerals to separate in the main crystallization are pyroxenes followed by calcium sodium, and potassium feldspars. If the magma is too dilute or too concentrated with respect to ions normally making up the pyroxenes and feldspars, other minerals may be formed. If the radii of the rarer elements are similar to the radii of the more common elements making up the minerals of the main crystallization stage, then in general these rarer elements will be diadochic with the more common elements and will occur as trace constituents of the main crystallization stage minerals. If the radii of the rarer elements are much greater or much less than the common elements, these rarer elements will accumulate in the final stages of crystallization where they often form typical minerals of their own. Thus the final crystallization stage involves cations and anions which were too large or too small to fit into the previously crystallized main mineral phases.

These final crystallization products are called pegmatites, and although their actual weight percentage in terms of the original magma is small, their economic importance is significant since the pegmatites are better differentiated and more readily accessible than are the products of the first and main crystallization weathering stages. (4)

Igneous rock when elevated to the Earth's surface is subject to weathering and sedimentation processes. The weathering of igneous rock is an important economic factor, for although 95% of our mineral resources come from the 5% which has undergone weathering.

Weathering of rock results from the action of various physical and chemical agents. Chemically speaking this weathering process might be compared to a selective extraction of certain ions ($\text{Na}(\text{I})$, $\text{Ca}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Mg}(\text{II})$) while other ions are left behind in the weathered residue (Fe_2O_3 , SiO_2 , TiO_2 , clay). The extracted ions are transported from the site of weathering and may be redeposited due to adsorption, hydrolysis, oxidation, precipitation by common ion effect, and precipitation due to evaporation of the solvent. In this type of differentiation process the concept of ionic potential (ionic charge: ionic radius) is omnipotent in determining the conjunction or codeposition of various elements. Thus, elements which do not codeposit from magmas due to size dissimilarities may be co-deposited in sedimentary rocks since their ionic potentials are nearly the same.

In disintegrating rocks the micas are consumed first, followed by feldspars, amphiboles, pyroxenes, quartz, and titanium minerals (9). Under ordinary weathering conditions both alumina and silica go into solution, the silica developing into a negative colloid, the alumina into a positive colloid. These oppositely charged colloids eventually form a gel which has the ability to adsorb cations from the surrounding solutions.



Cycles of the Alkali Metals

The alkali metals have been selected to illustrate specific examples of magma crystallization and weathering processes in the geochemical cycle. The alkali metals form a coherent chemical group, and with the exception of element 87 all of the alkali metals have stable isotopes occurring in nature. Sodium and potassium are among the main constituents of the upper portions of the Earth's crust; rubidium is an abundant trace element, but lithium and cesium are rare.

Abundance of alkali metals (g./ton) (9)

	<u>Li</u>	<u>Na</u>	<u>K</u>	<u>Rb</u>	<u>Cs</u>
Igneous rock	65	28,300	25,900	310	7

Lithium exhibits a number of anomalies in behavior when compared with the other alkali metals. It is the only alkali metal which does not enter the feldspar structure. Lithium is enriched in the later stages of magma crystallization as is evidenced by the fact that granites contain almost a hundred times lithium as do earlier crystallates. Li(I) replaces Mg(II) in minerals such as micas, amphiboles, and pyroxenes where both ions exhibit a coordination number of six.

In weathering processes lithium follows magnesium and tends to be carried to the sea where it is accumulated in marine sediments. Most of the industrial lithium supply is obtained from evaporates from Searles Lake, California.

The bulk of sodium and potassium found in igneous rock occur as feldspars. Sodium feldspars tend to crystallize out during the earlier stages of the main crystallization, while the potassium feldspars (especially K $[\text{AlSi}_3\text{O}_8]$) are characteristic of the later stages. Aside from feldspars the main carriers of sodium and potassium are the micas. However, whereas sodium and potassium feldspars are equally abundant, sodium micas are comparatively rare (e.g. paragonite). The common important micas are potassium minerals (e.g. biotite, muscovite). Sodium and potassium also occur in a large number of less geochemically important minerals.

Although both sodium and potassium go into solution during the original weathering processes, their geochemical courses from this point very widely. The smaller Na(I) ion is more highly hydrated than the larger K(I) ion---so much so that the hydrated Na(I) ion has a larger "effective radius" than the K(I) ion (a fact which is reflected by the ionic mobilities of Na(I) and K(I)). K(I) ions, upon initial weathering, are subject to preferential adsorption by clays and colloidal manganese hydroxide, while the protected hydrated Na(I) ions are not adsorbed to any appreciable extent. The bulk of sodium is carried to the sea. This differentiation during weathering is illustrated by the following table (8):

MATERIAL	<u>Na : K RATIO</u>
Igneous rock	1.09
Dissolved solids in lake and river H_2O	2.73

Dissolved solids in sea water	27.84
Argillaceous sediments (shales)	0.36

No marine evaporate salt minerals of $K(I)$ or $Na(I)$ show any appreciable degree of diadochic replacement by $Na(I)$ or $K(I)$ (i.e. sodium salts contain very little potassium and visa versa). On the other hand, $Na(I)$ and $K(I)$ despite appreciable size differences, show limited diadochic substitution in igneous rock, apparently due to the more open structure at the higher temperatures existing when igneous silicates were formed.

Rubidium and cesium tend to occur together in nature, usually following potassium with respect to their manner of occurrence. Due to their larger sizes, however, they exhibit a pronounced tendency to collect in the later stages of magma crystallization. Rubidium and cesium are capable of incorporation in feldspar structures and most potash feldspars contain some rubidium. Rubidium and cesium also occur in pegmatic potash feldspars and in micas.

Rubidium is about forty-five times as abundant as cesium, yet no independent rubidium mineral is known while cesium forms an independent mineral, pollucite ($Cs[AlSi_2O_6] \cdot H_2O$). Apparently the ionic radius of Rb^+ (1.48) is so close to that of K^+ (1.33) that the rubidium is camouflaged by the much more abundant potassium minerals. The radius of Cs^+ (1.67) is too large to permit appreciable camouflage by potassium minerals thus leading to the accumulation of cesium in the residual magma and the formation of the independent cesium mineral, pollucite.

Both rubidium and cesium go into solution during the initial weathering stage, but these elements show an even greater tendency for adsorption by clay than does potassium. They are almost completely removed in argillaceous sediments, and only a small portion ever reaches the sea and is incorporated in evaporates. Despite the small amount of rubidium and cesium in evaporates, this is still the most important commercial source for these metals.

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SOME MECHANO-CHEMICAL PROPERTIES OF WATER AND GLASS

Frank A. J. Moss

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Introduction

It is the purpose of this paper to discuss the borderline field and the relationship which exists between mechanical properties and chemistry, using some puzzling features of glass and water as examples.

The main difference between mechano-chemistry and photochemistry or electrochemistry is the fact that the application of energy in the form of light or electricity causes the material to undergo a change which can be recognized by chemical means. H. Eyring and his co-workers⁵ were the first to use chemical concepts for explaining mechanical phenomena, and they treated a flowing material in the same way as a mixture which undergoes a chemical change. The chemical nature of the substance has not changed by the process of viscous flow, but the breaking of existing bonds and the formation of new bonds is common to both.

In the past, such properties as viscosity, elasticity, or tensile strength were determined in terms of matter being a continuum, disregarding the atomistic point of view. The chemical approach considers the discussions of the ultimate building units, and there are cases in which only chemical aspects can provide an acceptable picture and in which a purely mechanical model fails.

Mechano-chemical phenomena are of scientific and practical interest in a variety of fields. Physicists, working in the field of ultrasonics; mechanical engineers, interested in corrosion effects produced by cavitation; medical scientists, interested in gas nucleation in blood, because gas emboli are a frequent cause of death among divers; chemical engineers, concerned with superheating phenomena of boiling water; all wish to know more about the mechanical properties of water.

The Mechanical Strength of Glass

Five factors are responsible for the unique mechanical properties of glass:

1. The shape factor

The thinnest glass fibres ever made were found to carry a load about one hundred times greater than was expected from strength tests made with thicker glass rods.

2. The time factor.

For short periods of time glass can support loads which are three or four times greater than those which they can support for longer times.

3. The temperature effect.

Glasses become mechanically stronger if tested at elevated temperatures. This is contradictory to what physicists have derived for the mechanical strength of matter as a function of temperature.

4. The influence of thermal treatment.

The mechanical strength of glass can be greatly increased by proper chilling. No other material can be improved to the same extent in its mechanical properties without detectable change of structure.

5. The influence of the environment.

A fibre of glass in vacuo is stronger than one exposed to air.

Weyl⁹ has explained these puzzling features by treating the phenomena from a chemical point of view, taking into account the specific way in which glasses respond to imperfections in their structures and the chemical reactions of the glass surfaces with the atmosphere.

It has been demonstrated that the tensile strength of glass can be compared with those of metals, plastics, and rubber, if these materials are tested under conditions in which their flaws and their environment exercise comparable influences.

Since it was found possible to explain the behavior of complex glasses by means of mechano-chemistry, and since glasses are similar to water in their structural peculiarities, the same approach has been applied in explaining some mechanical properties of water.

The Diffusion of Gases through Glass

The diffusion of gases through solids was treated originally as flow through molecular cracks, but this treatment proved insufficient to explain the results of modern work in this field. From a chemical standpoint, the gas molecule does not carry out a continuous motion, but jumps from place to place, and the kinetics of the process can be treated from the point of view of reaction rates. The activation energy corresponds to the energy required to squeeze through the electric fields of its neighbours. If strong forces are exerted on the diffusing units, the activation energy is high and the process is slow.

The chemical concept accounts for the fact that He diffuses faster through the oxygen network of a glass than does hydrogen, because the former has a smaller "chemical affinity" for the oxygen ions. The two gases have nearly the same diffusion speed if a solid is used which does not contain oxygen ions as a major constituent, e.g. rubber. Thus chemical inertness explains this phenomenon.

One can also examine the diffusion speed through glasses of the same composition but different heat treatment. Experiment shows that the chemical forces of a chilled glass are stronger and delay diffusion by increasing the activation energy.

The Abrasion Hardness of Glass

The chemical reactivity of the glass surface exerts a major influence upon the tensile strength of glass as measured by normal tests. The chemical aspect of the strength becomes more pronounced in going from macroscopic to microscopic dimensions, as in the grinding of glass, where the contact between the glass surface and the environment is much more intimate than in the tensile strength test. The abrasion hardness of glass gives additional evidence of the co-operation between mechanical and chemical forces.

The hardness of materials is a rather complex property which involves tensile strength and elasticity. Auerbach² found that it was impossible to apply to glass the hardness scale developed by Mohs. Applying the principle to glasses he found that they all scratch each other. Even the hardest glass could be scratched by a soft lead silicate.

The reason for this behavior is to be found in the work of Hardy and Hardy³, who state that the mutual scratching of two glasses is not a mere mechanical phenomenon but involves the formation as well as the breaking of chemical bonds. Clean glass surfaces sliding over one another combine chemically even at room temperature when brought under slight pressure. Pulling one glass surface over the other causes breakage of bonds, and as a result a scratch is formed. This property of clean glass surfaces to scratch each other is a constant source of annoyance and defects in the manufacture of glass and porcelain.

The great influence which the environment exerts on the strength of glass makes it obvious that grinding the glass in the presence of water is a process aided by hydrolysis. The abrasion hardness must therefore be influenced greatly by the chemical reactivity of the glass. This concept agrees with the observations that glasses of high chemical resistivity are harder to grind than other glasses which may have a higher indentation hardness. The work needed for creating the larger surface consists of the mechanical work necessary to break the primary bonds, minus the energy gained by the reaction of the new surface with its environment. Thus Engelhardt⁴ found that the grinding of quartz becomes more difficult if benzene is used instead of water, but easier if acetone or nitrobenzene are used. A rough estimate of the chemical energy available for participation in the abrasion process can be made from the heat of wetting by these liquids. It has been found that the addition of substances which will inhibit chemical reactions at the glass surface reduce the surface vulnerability, and use is made of this fact by the bottle-washing industries⁴.

The Fracture of Silicate and the Cavitation of Water.

Today it is well established that neither water nor silica contain single or polymerized molecules. There is no principal difference between the atomic structures of crystals and glasses of the same composition except that the ultimate building units repeat themselves regularly in crystals and randomly in glasses. Silicate crystals and glasses both form 3-dimensional networks of SiO_4^{4-} tetrahedra which are closely interlinked by having oxygen ions in common.

So far as the atomic structure of water is concerned, Bernal and Fowler³ have emphasized that mere dipole association of H_2O molecules will not explain the abnormal density of water, its behavior under pressure and the fact that it possesses (as does silica glass) a negative thermal expansion in a certain low temperature region. The peculiar cohesion of water molecules is due to the geometrical possibility of the fitting together of the H_2O molecules. The presence of two H atoms per molecule gives the possibility of attaching two molecules by this means and two others by means of their own H atoms. This structure is then similar to the ionic structure of quartz, with one H between every two oxygens instead of one oxygen between every two silicons.

If a piece of glass is treated as a single huge molecule, then its breakage must be considered a chemical process, a dissociation of this molecule. The cleavage would produce two chemically unsaturated or electrically charged units. The cleavage of a mica crystal can be cited as an example where the electric charges are so strong that sparks can be seen in the dark. Due to reaction with moisture the new surfaces soon become hydrated and the hydration energy of the two fragments aids the mechanical rupture.

The same mechano-chemical treatment of the fracture of glass can be applied to the cavitation of water. Cavitation produces a new surface, and exposes H and O atoms which are electrically charged or chemically unsaturated. In an ultrasonic field the fractured and dissociated water recombines, the mechanical vibrations having been converted into heat partly via heat of neutralization. If the water, however, contains other substances such as dissolved oxygen or potassium iodide, other chemical reactions become possible.

In the dark, cavitation can be seen by the luminescence which accompanies the recombination of the broken water molecule. It can be compared with the luminescence observed on cleaving mica, or with the type of chemiluminescence described by R. Audubert¹ on neutralizing strong acids with strong bases. The same luminescence can be produced by shaking a degassed glass powder in an evacuated tube, or breaking a lump of sugar.

If the strength of glass is determined markedly by the presence of flaws, then the same must be true for water under hydrstatic tension. Water containing microscopic or submicroscopic gas bubbles cavitates more easily than water which has been thoroughly degassed. The bubbles initiate a break in the structurê. Gas supersaturation in water can be released by the addition of non-polar crystallized substances, e.g. PbI_2 , or by treatment of the containing glass surfaces with solutions of mercuric or lead salts.

Mechano-Chemical Phenomena in the fields of Electrochemistry and Explosives.

In the field of electrochemistry the mechano-chemical properties of water play an important role. The term "overvoltage" is used to explain the discharge of some metals, from aqueous solution, which theoretically should not be precipitated. From a mechano chemical viewpoint the overvoltage arises from the work connected with the breakage of the bonds between the water and the electrode material, and includes the forces which have to be overcome before a gas bubble can form.

The physics of explosives is another field where the principles of mechano-chemistry are being applied. The purely mechanical approach has failed to explain the fact that nitroglycerin gelatin can explode with two different velocities, depending on the nature of the detonator⁷. It has been suggested that consideration of the problem in molecular dimensions might afford a solution. Similar problems include the explosion of NI_3 by certain sound waves, and the detonation of $\text{Hg}(\text{No})_2$ crystals.

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OBSERVATIONS ON THE HYPOPHOSPHATES OF THORIUM AND THE RARE EARTHS

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Thorium hypophosphate was first described by Kauffman in 1899(1). The compound received immediate attention because of its exceedingly slight solubility in water and in both dilute and concentrated acids and alkali. The possibility of using this compound for quantitative separations was recognized when it was reported that the rare earth hypophosphates were soluble at comparatively low acid concentrations.

A radiometric method of analysis for the determination of thorium in the presence of the rare earths was recently developed by Moeller and Schweitzer (2). The procedure is based upon the precipitation of thorium from solutions 0.3N, in acid by the addition of a known amount of standard radioactive pyrophosphate solution. The radioactivity removed from the solution is proportional to the quantity of thorium in the sample. The usefulness of the procedure is limited, however, since the acidity must be carefully controlled in order to obtain clean-cut separations of thorium from the other substances present in the solution. A consideration of the chemistry of hypophosphoric acid suggested that the precipitation of thorium as the hypophosphate might also be made the basis of a radiometric method.

Before undertaking the actual investigation of the radiometric procedure for analysis, it was considered advisable to make some preliminary studies on thorium and the rare earth hypophosphates. It was necessary to prepare the compounds, to verify their compositions, to determine their relative solubilities, and also to establish the approximate pH values at which the compounds precipitate. In addition, it became obvious during the course of the investigation that adsorption and peptization phenomena were causing difficulties in the procedure. Therefore, the colloidal properties of these compounds were also studied.

It is not possible to undertake a study of the hypophosphates of thorium and the rare earths without first considering the chemistry of hypophosphoric acid and its salts. Hypophosphoric acid was first reported by Sälzer(3) in 1877. It is prepared by partially submerging sticks of white phosphorus in water and allowing air to have limited access to the mixture, (4,5,6) by the action of hot nitric acid solutions of silver or copper on white phosphorus (7,8,9), by the anodic oxidation of copper phosphide in two percent sulfuric acid solution, and by allowing red phosphorus to react with sodium hypochlorite (10,11) or sodium chlorite solution (12). The radioactive hypophosphate used in this investigation was prepared by the red phosphorus-sodium chlorite reaction. The acid is usually isolated as the slightly soluble disodium salt, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$. The formula for hypophosphoric acid is represented by $\text{H}_4\text{P}_2\text{O}_6$. It has been established that the acid is dimeric. Hypophosphoric acid decomposes when gently heated into phosphorus and phosphoric acid. Solutions of the acid undergo similar disproportionation.

The acid is not an active reducing agent and is not oxidized by the halogens, nitric acid or even boiling dichromate. Hypophosphoric acid has no acid anhydride. Thorium, yttrium and neodymium hypophosphates were prepared by treating solutions of the salts of these metals with solutions of disodium hypophosphate. X-ray studies showed that even after long periods of digestion the thorium hypophosphate precipitate did not become crystalline. The neodymium and yttrium hypophosphates gave powder patterns which were characteristic of crystalline materials.

Conductometric titrations were found to be useful for the determination of the compositions of these compounds. It was indicated that the thorium compound corresponds to the formula, ThP_2O_6 , whereas the neodymium and yttrium compounds are represented by $(\text{RE})_4(\text{P}_2\text{O}_6)_3$. It was interesting to find that when these titrations were carried out in alcoholic solution (30% ethyl alcohol) a reaction took place between the hydrogen ions in solution and any excess hypophosphate which was added. It appeared that this reaction was an acid-base reaction in which molecular hypophosphoric acid was the reaction product. The removal of hydrogen ions from the solution was indicated also in pH titrations.

A wet chemical method of analysis was also developed for the determination of the composition of thorium hypophosphate precipitates. In this procedure thorium hypophosphate was dissolved in a solution of cerium (IV) in 1 N nitric acid. By determining the quantity of cerium solution in excess, it was possible to calculate the amount needed for the oxidation of phosphorus(IV) to phosphorus(V) and finally the hypophosphate in the compound. The thorium in solution was precipitated, along with the cerium, as the oxalate and was ignited to the oxide. Since the quantity of cerium present was known, the weight of thorium in the mixed oxide was determined. The results showed that thorium and hypophosphate reacted in a 1/4 mole ratio. The procedure was extended to include the yttrium and neodymium compounds, but these were not soluble in the nitrate-cerate solutions. A modification of the procedure permitted these analyses but the results obtained were not good. Neodymium-hypophosphate ratios of 4.8 to 3 and yttrium-hypophosphate ratios of 4.6 to 3 were found.

The solubilities of thorium and rare earth hypophosphates were determined radiochemically, and the order of solubility was 10^{-4} molar. The solubilities increased in the order--thorium, neodymium, yttrium. The solubility measurements indicated that the thorium could be separated from the rare earths by precipitation of the thorium as the hypophosphate from strongly acidic solutions. Therefore, it was attempted to develop a radiometric procedure for determination of thorium in the presence of the rare earths, employing this separation as a basis. Radiometric analyses for thorium were run on pure thorium solutions in about 4N hydrochloric acid with radioactive hypophosphate. It was found that in low thorium concentrations, 9 mg. or less per fifty milliliters of solution, the thorium detected was less than that added. In concentrations greater than this, the thorium detected was greater than that added. The addition of electrolyte had little effect on these

values. Heating the samples at various temperatures magnified the errors in the low concentrations, and it was found that, when samples were heated at 85°C. for three hours, low results were observed for those containing less than thirty-five milligrams of thorium. In greater concentrations, high results again were obtained, but to a lesser extent. Experiments showed that the thorium hypophosphate adsorbed hypophosphate ion. Highly charged cations were added to these solutions in order to induce competition for the surface of the precipitate, but this had no effect on the results. It was concluded that a radiometric method for the determination of thorium as the hypophosphate was not practical.

It was noted during the course of the investigation that thorium hypophosphate colloids were formed when thorium hypophosphate precipitates suspended in acid solutions were treated with large quantities of thorium salt solutions. These colloidal systems were studied in the ultracentrifuge, and calculations using the classical equations of Svedberg showed that the average diameter of these particles, prepared under the given set of conditions, was about 30A. It was also observed that, when thorium nitrate solutions were run in the ultracentrifuge at speeds between 29,000 and 50,000 r.p.m. the thorium ion was sedimented appreciably. The observed sedimentation was very nearly that which was calculated from the classical ultracentrifuge equations.

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STUDIES ON THE STABILITY OF INORGANIC COMPLEX COMPOUNDS

I. METAL CHELATES OF TRIKETONES

Richard Lee Dalton

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Chelate compounds have received considerable attention because of their unusual stability, and, in the case of inner complex compounds of the 1,3-diketones, because of their high degree of covalent character. Important information concerning the nature and stability of chelate compounds may be gained by studying the properties and structures of the metal derivatives of the triketones. The copper complexes of numerous triketones have been prepared¹⁻⁷ and in most cases, found to possess the properties typical of inner complexes. However, no attempt has previously been made to determine the structures of the metal derivatives of the triketones.

The copper(II) and nickel(II) complexes of di-enolic 2,4,6-heptanetrione were found to contain one ketone molecule per metal atom. The copper complex formed unstable addition products with ammonia and pyridine containing one molecule of base per molecule of complex. A stable addition product of the nickel compound was found to contain two molecule of pyridine and one-half molecule of water per metal atom. None of the above complexes had an unbonded carbonyl group as shown by their infrared spectra. Their structure must be one in which each metal atom is bonded to a carbonyl oxygen and a hydroxyl oxygen of one triketone molecule, forming a "resonating" chelate ring, and to a hydroxyl oxygen of a second triketone molecule, perhaps to form a dimeric compound.

The method of continuous variations was used to show that iron(III) chloride and 2,4,6-heptanetrione form two colored complexes containing metal to ketone ratios of one to one and one to two.

Complexes of copper(II), cobalt(II), nickel(II), iron(II), and manganese(II) with 3-acetyl-2,4-pentanedione and of the first three metals with 2-benzoyl-2,4-pentanedione were found to contain two molecules of ketone per metal atom. The properties of these compounds were typical of inner complex compounds. The copper complex of the first triketone sublimed unchanged in a vac um. Both cobalt complexes and the manganese complex of the first triketone added two molecules of pyridine per metal atom. The nickel and cobalt complexes were shown to be isomorphic by their X-ray diffraction patterns. The infrared spectra of all of these metal derivatives had adsorption peaks attributable to an unbonded carbonyl group.

Apparently the structure of these mono-enolic triketone complexes is one in which each triketone molecule forms one chelate ring, analogous to that formed in the complexes of the 1,3-diketones, and one carbonyl group remains unchanged. Because of the phenyl group in the complexes of 3-benzoyl-2,4-pentanedione the adsorption peak due to the unbonded carbonyl group was shifted 45-cm^{-1} from

its position in the spectra of the compounds of 3-acetyl-2,4-pentanedione, and the rate of hydrolysis to give the corresponding complexes of 1-phenyl-1,3-butanedione and 2,4-pentanedione was greatly increased.

The lack of an adsorption peak in the region 1600-1750 cm^{-1} in the spectrum of the potassium salt of 3-acetyl-2,4-pentanedione indicates that all three oxygen atoms are bound in some manner to the potassium ion.

It is suggested that the infrared band attributed to the carbon-oxygen bond in the chelate ring may be used to indicate the relative stabilities of metal complexes of the same ketone.

II. CIS-TRANS INTERCONVERSION OF DICHLOROBIS(PROPYLENEDIAMINE) COBALT(III) CHLORIDE

The interconversion of cis-trans isomers of inorganic complex compounds has received special attention because of its relationship to a study of the mechanism for the replacement of coordinately bound ligands. Any theory which can logically explain the numerous examples of such interconversions must consider the mechanism of substitution and should, therefore, pave the way for further work to establish this mechanism by more quantitative methods. The present work was undertaken to study the interconversion of the cis-trans isomers of dichlorobis(propylenediamine)cobalt(III) chloride in the solid state, with a view toward suggesting a mechanism for these transformations.

It has been shown that cis dichlorobis(propylenediamine)cobalt(III) chloride 1/2-hydrate will undergo conversion in the solid state to the trans isomer in twenty-four hours if ground to a fine powder and not perfectly dry. For this change the cis isomer must be in an amorphous state, which is produced when the hydrochloride of the trans form is heated to 105°C. for twelve hours. Since water is required, it is suggested that the conversion takes place by the intermediate formation of a chloro-aquo complex. The change cannot be due to a difference in solubility since the cis form is the less soluble one. The theory of "backside" approach as suggested by Basolo⁸ will explain the conversion since a group approaching a face or edge of the imaginary octahedral structure opposite the group being replaced may occupy a position cis or trans to the other monodentate group. If there is a difference in the stability of the two forms, the final product should be the more stable one.

It has been shown that the trans salt must be in the form of the hydrochloride to be converted into the cis isomer upon heating. Samples of the trans salt without hydrogen chloride, prepared by three different methods, did not change under the same conditions.

The theory of "backside" approach of the incoming group gives the only satisfactory explanation since such a mechanism must always give the cis form from the trans form.

An important consequence of this mechanism of conversion is that there must be an exchange of ionically and covalently bound chloride ions. This could be established definitely by the use of radioactive chlorine to trace the course of the chloride ions in this conversion.

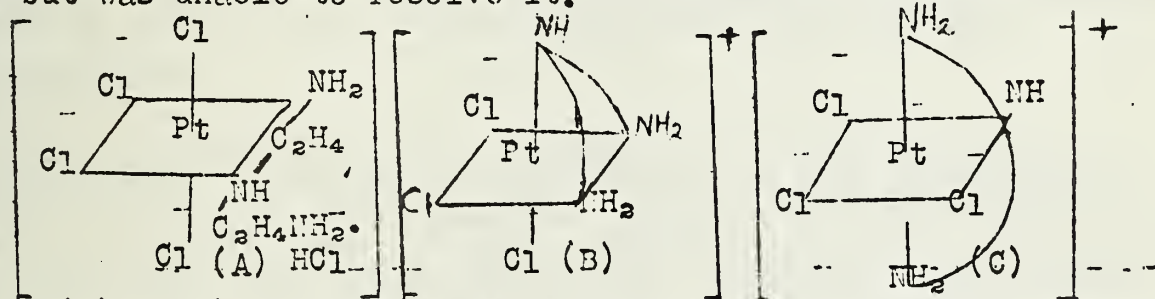
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INTRODUCTION

The problem of resolving into optically active antipodes compounds containing properly substituted nitrogen atoms has attracted interest for a number of years. Because of the established tetrahedral configuration of the nitrogen atom, early workers attempted resolution of unsymmetrical tertiary amines, but met with no success. It is currently believed the failure in these cases was due to the rapid vibration of the nitrogen atom through the plane of the three substituents, the calculated energy for such a change being less than the stability requirements for resolution of the optical isomers (1). Consequently, it was postulated that if a fourth group were attached to the nitrogen atom through its unused electron pair, the tetrahedral configuration could be fixed, and, the four groups being different, these compounds would be resolvable. This has been proved by the resolution of various unsymmetrical quaternary ammonium salts and tertiary amine oxides.

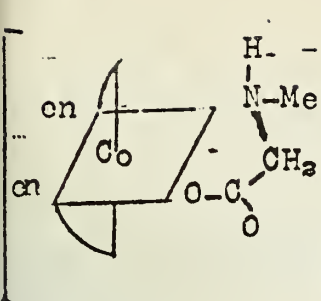
Extensions of the latter scheme to the field of complex compounds have been made by coordinating a substituted nitrogen compound to a metal ion. Mann (2) used *E, E*-diaminodiethylamine (diethylenetriamine) and prepared tetrachloro(*N, N'*-diaminodiethylamine monohydrochloride) platinum (IV) (A), which contains an asymmetric nitrogen atom, but was unable to resolve it.



Mattern (3) later concluded that diethylenetriamine acts here as a tridentate group and that Mann's compound could likely have been either of the isomeric structures (B) or (C), both of which possess a plane of symmetry and are thus not resolvable.

Meisenheimer (4) first reported successful resolution of the *N*-methylglycine (sarcosine) cobalt complex (D); however, as his evidence was not positive, and as Basolo (5) was not able to repeat his work, the validity of the results was open to question. Basolo also prepared other cobalt- and platinum- sarcosine complexes but was in no case able to obtain any resolution.

In each of the above examples, one of the four "groups" about the nitrogen is a hydrogen atom. It is now believed that in such cases the hydrogen atom is labile enough to ionize to a slight extent, thus causing continuous racemization of the optical forms.



It seems quite reasonable that this process occurs in the above complexes, since Block (6) was able to treat the bis-ethylenediaminegold (III) ion, $Au(en)_2^{+3}$, with one equivalent of base and form $Au(en)(en-H)^{+2}$ in which one hydrogen atom has been replaced. ("en-H" represents $NH_2CH_2CH_2NH-$)

In the light of the foregoing results, it was thought the use of a nitrogen compound containing three different substituents, other than a hydrogen atom, would offer a greater possibility of resolution. Consequently, N-methyl-N-ethylglycine was selected as a coordinating agent for preparing and demonstrating the optical activity of metal complexes containing an asymmetric nitrogen atom. It was realized that, although such complexes would be more optically stable, the tertiary nature of the nitrogen atom would decrease its tendency to form a coordinate bond with a metal ion. However, the possibility of chelation through the carboxyl group, involving formation of a five-membered ring, was expected to largely overcome this disadvantage. In addition, it seemed desirable to synthesize a compound in which the type and configuration of the other ligands offered no possibility of optical isomers, so that the activity, if found, would necessarily be due to the nitrogen atom alone.

Attempts have been made to prepare various cobalt(III) and platinum(II) complexes fitting the foregoing specifications, but the only success that has been achieved has been with platinum.

COBALT COMPLEXES

A attempted replacement under a variety of conditions of the chloride, ammonia, or sulfite, respectively, in $cis-Co(NH_3)_4Cl_2^{+}$, $Co(NO_3)_4(NH_3)_2$, and $Co(NH_3)_4(SO_3)_2$ by the amino acid was unsuccessful. In every case, either no reaction occurred or the experimental conditions (pH, temperature, etc.) decomposed the cobalt complex, in time, to cobaltic hydroxide or cobaltous salts.

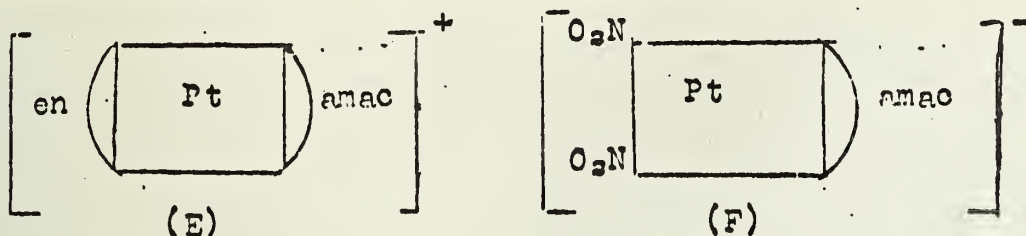
Furthermore, the amino acids, glycine, sarcosine, and N,N-diethylglycine, were made to react with cobaltic hydroxide to determine the effect of substitution of the nitrogen atom on complex stability. Glycine forms a very stable tris-complex. Evidence of an analogous, but less stable, sarcosine complex was obtained, although the compound was never isolated in a pure form. The distributed glycine, however, showed no reaction.

It was concluded that the tertiary nitrogen, even though aided by the possibility of chelation, was not capable of forming a stable cobalt-nitrogen bond.

PLATINUM COMPLEXES

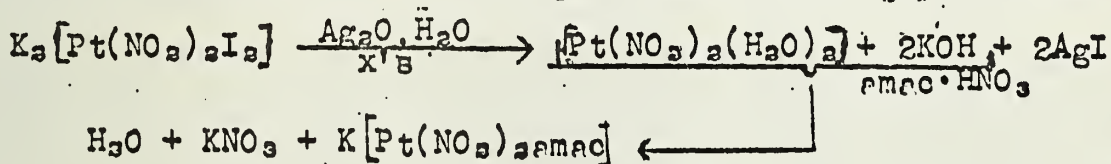
Platinum(II) was selected as a central ion because its higher nuclear charge offered possibility of a stronger metal-nitrogen bond, and also simpler complexes were possible with the four-covalent, planar structure.

The amino acid reacts with potassium tetrachloroplatinate(II) to form the bis-amino complex, $[Pt(amac)_2]$ ("amac" represents the coordinated amino acid). However, as this is a non-electrolyte, attempts were made to prepare an ionic complex which could be resolved by salt formation with an optically active ion. Consequently, the reactions of the amino acid with $[Pt(en)Cl_2]$ and $K_2[Pt(NO_2)_2I_2]$ were investigated in the hope that the halides could be replaced to form either (E) or (F)



No success has yet been attained by trying to replace the two chlorides from $[Pt(en)Cl_2]$. This may be because they are attracted more strongly by the central ion than the amino acid, and, too, there is no trans effect operative here to make the chlorides more labile as in the case of the tetrachloroplatinate(II) ion.

An ionic amino acid complex has been prepared from potassium diiododinitroplatinate(II) according to the following procedure:



In the preceding exploratory experiments, the amino acid used was N,N-diethylglycine because of the availability of the starting material and its ease of preparation as contrasted to N-methyl-N-ethylglycine. However, potassium dinitro (N-methyl-N-ethylglycine) platinate(II) has been prepared in a manner analogous to the diethyl compound.

To date, the resolution studies have not been undertaken.

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ELECTROCHEMICAL STUDIES ON NON-AQUEOUS SOLUTIONS OF RARE EARTH SALTS

Paul Zimmerman

May 29, 1951

I. Introduction:

Chemists have from time to time chided themselves for their servitude to water as a solvent for inorganic compounds, but they have for the most part remained willing slaves to water. On occasion however, goaded by the failure of water chemistry in some respect or other, they have looked with a wayward eye to non-aqueous solvents. Such has been the case in the field of electrochemistry. Chemists have been intrigued by the possibility of plating out of non-aqueous solvents metals which cannot be deposited from solutions of their compounds in water. As early as 1904 Kettembeil explored the possibility of depositing metals from solutions of their salts in pyridine and in absolute alcohol. (5) During the half-century a rather small number of chemists, widely scattered, have followed Kettembeil's banner with more or less persistence. Among the vanguard of these were Dr. Hopkins and Dr. Audrieth at the University of Illinois. They and their students explored the solubilities and electrochemical properties of anhydrous rare earth compounds in a variety of solvents.

In 1938, K. Kobe and G. Putnam reported on their studies of ethylenediamine as an ionizing solvent. (6) They claimed to have electrodeposited on copper from this solvent such active metals as magnesium, lithium, sodium and potassium. In view of this it appeared to the present investigators that it might be worthwhile to explore the value of ethylenediamine as a solvent for anhydrous rare earth compounds. It seemed plausible that a basic solvent, being itself an electron pair donor, might be a suitable medium for the preparation and stabilization of rare earth metals. Since T. Dirkse and H. Briscoe reported the deposition of metallic aluminum, magnesium, and other metals from ethanolamine, it was decided to study this basic solvent also. (3) Morpholine, a kindred compound, was also included in our studies.

II. Experimental:

A. Solubility Studies:

It was found possible to dissolve anhydrous rare earth compounds in the solvents studied. With the exception of but one compound, ethanolamine is the best solvent. Ethylenediamine may be classed as a fair solvent for the compounds studied. Morpholine was found to be a poor solvent.

The acetates of neodymium and yttrium were found to be much more soluble than the respective halides of the metals. The iodide of neodymium is more soluble than the bromide in both ethylenediamine and morpholine. This is in accord with expectations based on theory and observations of the behavior of compounds in such solvents as liquid ammonia. Ethanolamine exhibits a reverse

trend, however. In it the bromide is more soluble than the iodide. It is interesting that Isbin and Kobe observed the same phenomena with respect to the solubilities of sodium bromide and sodium iodide in ethanolamine. (4) Although it has not yet been measured quantitatively, the solubility of lanthanum nitrate in ethylenediamine appears to be of the order of that of neodymium bromide.

B. Conductivity Studies

Conductance measurements show that ethanolamine is the best ionizing agent of the three solvents. Ethylenediamine is a fair ionizing solvent; whereas morpholine is a poor one. This, too, is to be expected from the degree of polarity possessed by the respective solvents. The acetates proved to be poor electrolytes in the solvents studied. The nitrates, bromides, and iodides are good electrolytes.

It is of interest that in both ethanolamine and ethylenediamine yttrium acetate, at a given concentration, possesses a slightly higher equivalent conductance than does neodymium acetate. This is contrary to expectations, since the slightly larger neodymium ion should more readily dissociate from the acetate ion. However, Burgess and Kraus observed similar anomalies in pyridine solutions. (2) It seems logical to attribute it to the smaller ion being more acid in nature and thus forming a more stable bond with the basic molecule of the solvent. Burgess and Kraus feel that because of this the ion may remain solvated even in the ion pair, thus forming an effectively larger cation which would contribute to the more ready dissociation of the ion pair.

The effect of the variation of temperature on the conductance of the respective solvents and the conductance of solutions was studied. The addition of water in small amounts was found to increase the conductance of the solution. This may be due to the water molecules taking the place of ethylenediamine in the solvated ion. The resulting ion would be smaller and hence more mobile. However, the explanation may lie in the increase in the dielectric constant of the solution with the addition of water.

C. Electrodeposition Studies

Smooth, thin, lustrous, metallic appearing plates containing yttrium and neodymium respectively were obtained from ethylenediamine solutions of the acetates, bromides, and iodides. Platinum anodes and cathodes were used. The yttrium deposits varied in appearance from black to iron gray. With one exception the neodymium deposits were of a yellow, golden tinge. Unfortunately, due to the high resistivity of the solutions, the plates obtained weighed in each case only a few milligrams. This made their characterization extremely difficult.

The yttrium deposits possessed the following properties:

1. The material was turned white by prolonged exposure to water.
2. Dilute hydrochloric acid dissolved the material rapidly with the evolution of hydrogen.

3. The material very readily reduced potassium permanganate to the manganous ion.
4. Gravimetric procedures, though admittedly inaccurate because of the small amounts of materials available, indicated the elemental yttrium content of the plate to be of the order of 50%.
5. The microanalyst reported that the material either picks up water or oxidizes extremely rapidly. Further, the material apparently reduces the vanadium catalyst used in the microanalysis.
6. Microanalysis indicated that the amount of carbon, hydrogen, and nitrogen in the plates varied. No consistent values were obtained. It appears most reasonable to attribute the presence of these elements in the deposit to the adsorption of the solvent and to reaction of the plate and the adsorbed solvent with atmospheric water and carbon dioxide. In no case did the values of C, H, N run high enough to indicate the deposition of a complex.
7. X-Ray diffraction patterns obtained from the yttrium plate were entirely different from those of the acetate, oxide, or hydrous oxide. The rings were of small diameter, thus indicating a material with high "d" spacings. The pattern is unlike that obtained by Quill from yttrium produced by the electrolysis of a fused melt of an alkali salt and the yttrium chloride. (7) However, this in itself does not rule out the possibility of the deposit containing metallic yttrium since lanthanum, cerium, and praseodymium all exist in two crystalline forms. Furthermore, other metals, e.g. chromium, tungsten, when prepared by an electrolytic method may possess a different type of crystal structure. (8)

The neodymium deposits possess in general the same properties as do the yttrium deposits. Microanalysis of one sample showed the material to contain 6.1% carbon, 3% hydrogen, 4.64% nitrogen. These values are too low to correspond to any likely metal complex compound.

The reducing power of the neodymium deposits from neodymium bromide in ethylenediamine was studied quantitatively by means of acidified potassium permanganate. The number of milliequivalents accounted for by the reducing power of the sample was thus determined, and the reducing power was expressed on a percentage basis using metallic neodymium as a standard. Despite the fact that the plate contained adsorbed solvent and was exposed, despite all precautions, to a certain amount of oxidation, reducing power values were obtained ranging from 28 to 78 percent compared to neodymium metal as 100%. It is noteworthy that if one postulates formulas for various neodymium compounds which might conceivably be present in the deposit, the only compounds that readily come to mind and that possess reducing power in this range would contain neodymium in the plus one oxidation state. It seems more reasonable to conclude that the plate contained metallic neodymium than to assume that neodymium can exist in a plus one oxidation state.

Of late it has been found possible to obtain somewhat heavier deposits by electrolyzing neodymium iodide in ethylene diamine. It is hoped that it will be possible to obtain enough of the material to characterize it more satisfactorily.

Polarographic experiments were carried out but the results were inconclusive.

The only deposit obtained from ethanolamine was from the electrolysis of the acetate. It was present in small amount, was white filmy and floated on top of the solution. It was assumed to be the solvated oxide.

Morpholine solutions possess such high resistance that no attempt was made to electrolyze them.

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The following is the abstract of a talk given before the seminar by Professor Jonassen on February 20, 1951.

INORGANIC COMPLEX COMPOUNDS CONTAINING POLYDENTATE GROUPS VI.
FORMATION CONSTANTS OF COMPLEX IONS OF DIETHYLENETRIAMINE
AND TRIETHYLENETETRAMINE WITH DIVALENT IONS.

By

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The formation curves and formation constants of the complex ions formed between diethylenetriamine (abr. dien) and triethylenetetramine (abr. trien) and the following metal ions: Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) have been determined at 30° and 40°C. The pH method developed by Bjerrum was used to determine these quantities.

Heats of formation and free energies of formation have been calculated from these data.

All the divalent ions investigated except the copper(II) and zinc(II) ions show a coordination number of six. The formation constants of copper(II) and zinc(II) ions with dien indicate that these two ions coordinate two tridentate dien molecules, but that not all of the three amino nitrogen atoms of the second dien partake in the bonding.

In the case of trien these two ions only complex with one quadridentate trien molecule. All the other metal ions investigated form binuclear complexes with trien of the type $M_2A_3^{+4}$.

The order of stability of these complexes follow the second ionization potential of the gaseous atoms as was previously shown for other complex ions by Calvin and Melchior.

The formation constants obtained in this investigation shown that the expansion of the coordination number to six in the tetramine complexes produces a smaller increase in stability than the corresponding increase in the dien complex ions. This is probably due to the formation of the binuclear complexes in the tetramine series.

Table I gives the pK_a of the two amines. Table II gives the data for the determination of the Formation Constant of the Mn(II)-dien complexes and Tables III and IV give the thermodynamic data for all the complexes investigated.

TABLE I

BASE CONSTANTS OF POLYAMINES

	pK trien	
	30°	40°
pK ₁	3.82	3.76
pK ₂	7.01	7.79
pK ₃	9.36	9.14
pK ₄	9.99	9.76
	pK dien	
	30°	40°
pK ₁	4.78	4.59
pK ₂	9.94	8.94
pK ₃	9.94	9.68

TABLE II
FORMATION CONSTANTS OF MANGANESE (II) AND
DIETHYLENTRIAMINE AT 30° C.

$$= - \log \left(\frac{1 + (2 - \bar{n}) \text{ dien } k_2}{(1 - \bar{n})} \right)$$

\bar{n}	p dien	$\log \frac{\bar{n}}{1 - \bar{n}}$		$\log k_1$
0.153	4.80	-0.74	-0.01	4.05
0.349	4.29	-0.27	-0.04	3.98
0.400	4.19	-0.18	-0.05	3.96
0.549	3.97	+0.09	-0.09	3.98
0.683	3.80	+0.33	-0.16	3.97
0.804	3.66	+0.61	-0.28	3.93
Average				3.99

\bar{n}	p dien	$\log \frac{\bar{n} - 1}{2 - \bar{n}}$		$\log k_2$
1.099	3.28	-0.96	+0.50	2.82
1.293	3.07	-0.58	+0.19	2.88
1.468	2.80	-0.06	+0.08	2.82
1.640	2.55	+0.25	+0.04	2.84
1.777	2.24	+0.54	+0.02	2.80
Average				2.83

TABLE III

THERMODYNAMIC VALUES FOR COMPLEX IONS OF DIETHYLENETRIAMINE AND DIVALENT METAL IONS

Cation	T°C	log K ₁	log K ₂	log K _n	-ΔCF ₁	-ΔF ₂	-ΔF _N	-H ₁	-ΔH ₂	---H _N
Mn(II)	30	4.0	2.8	6.8	5.5	3.9	9.4	4.3	4.3	8.6
Mn(II)	40	3.9	2.7	6.6	5.6	3.9	9.5			
Fe(II)	30	6.2	4.1	10.5	8.6	5.6	14.2			
Fe(II)	40	6.0	3.0	9.9	8.7	5.6	14.3	8.7	8.7	17.4
Co(II)	30	8.5	6.1	14.6	11.8	8.5	20.3			
Co(II)	40	8.3	5.8	14.1	12.0	8.5	20.5	8.7	13.0	21.7
Ni(II)	30	10.8	8.1	18.9	15.0	11.2	26.2			
Ni(II)	40	10.5	7.8	18.3	15.2	11.2	26.4	13.0	13.0	26.0
Cu(II)	30	16.1			22.4					
Cu(II)	40	15.6			22.4			21.5		
Zn(II)	30	9.1			12.1					
Zn(II)	40	9.0			13.0			4.3		

TABLE IV
THERMODYNAMIC VALUES OF COMPLEX IONS OF TRIETHYLENEDIAMINE AND DIVALENT METAL IONS

Complexion	T°C	log K_1	log $K_{s:2}$	log K_N	-F ₁	-ΔF _{s:2}	-ΔF _N	-ΔH ₁	-ΔH _{s:2}	-ΔH _N
Mn(II)	30	5.4	2.8	8.2	7.5	3.9	11.4	'	'	'
Mn(II)	40	5.3	2.7	-8.0	7.6	3.9	11.5	4.3	4.3	8.6
Fe(II)	30	8.3	3.9	12.1	11.5	5.4	16.9	'	'	'
Fe(II)	40	8.1	3.7	11.3	11.7	5.3	17.0	8.7	8.7	17.4
Co(II)	30	11.2	3.4	14.6	15.5	4.7	30.2	'	'	'
Co(II)	40	11.0	3.3	14.3	15.8	4.7	30.5	8.6	8.3	13.0
Ni(II)	30	14.3	5.6	19.9	19.8	7.9	27.6	'	'	'
Ni(II)	40	14.0	5.4	19.4	20.1	7.8	27.9	13.0	8.7	21.7
Cu(II)	30	20.6		20.6			28.6			
Cu(II)	40	20.1		20.1			28.8			21.7
Zn(II)	30	11.9		11.9			16.5			
Zn(II)	40	11.8		11.8			16.9			4.3
Cd(II)	30	10.9	3.1	14.0	15.1	4.3	19.4			
Cd(II)	40	10.8	3.1	13.8	15.5	4.4	19.9	4.3	4.3	8.7

* All values in K cal/mol.

ΔH values = ΔH 308°

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